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PERMANENT ADDRESS:

15/4A, Raja Manindra Road
Calcutta-37, WEST-BENGAL
INDIA

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NEW DEVELOPMENTS IN SEMI-EMPIRICAL MOLECULAR ORBITAL THEORY

by

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A THESIS

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The undersigned certify that they have read, and recommend to the Faculty of Graduate Studies and Research, for acceptance, a thesis entitled

NEW DEVELOPMENTS IN

SEMI-EMPIRICAL MOLECULAR ORBITAL THEORY

submitted by ARCHANA DASGUPTA in partial fulfillment of the requirements for the degree of Master of Science.

S. Huzinaga
Supervisor

Alan

Jaan W. Linn

Satya Jaal

Date September 10, 1973

TO MY PARENTS

ABSTRACT

In a recent review article on the semi-empirical all-valence-electron method, Klopman wrote of ".... the painful dilemma of having to choose between a method that gives good heats of formation and poor bond distances, or poor heats of formation and good bond distances. ... Its solution, if it can be found, would probably be the most important contribution in the field of semi-empirical calculation of large molecules."

We have set out to meet the challenge. In the present thesis, the first stage of our effort will be described and moderately successful numerical results will be reported. We start with a critical review of the past developments of the subject and the fundamental theoretical background and then proceed on to the description of a new approach to the subject.

A careful analysis of the total energy of molecular systems has led us to the point of view that a proper balancing mechanism between contributions from the one-electron and two-electron parts of the total energy is vitally important in order to obtain good heats of formation and good bond distances. Keeping this goal in mind, we have introduced a method at the CNDO-level which

has some new features. A new formula for estimating coulomb integrals has been proposed here. This formula introduces two new parameters which have sufficient flexibility to continuously cover the rigorous formulas of Roothaan or the approximate formulas of Ohno and Mataga-Nishimoto. Another new feature is the way in which the one-electron part of the Hartree-Fock operator is parametrized. The potential of these new parameters for achieving the flexibility needed to accomplish the required delicate balance is greater than that in previous CNDO methods.

Our computer program is constructed at the level of so-called CNDO (Complete Neglect of Differential Overlap) level, but it is much more flexible in many respects than the widely distributed CNDO/2 computer program.

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Chapter I

INTRODUCTION

Although for nearly fifty years the principles of quantum mechanics, which are necessary for the understanding of the electronic structure of molecules, have been known, still it has been only in recent years that great advances in ab initio calculations of molecular electronic structure[1] have been achieved. In spite of these recent achievements, ab initio calculations are of limited use since they are very expensive and require large computation time. Even if we spend hundreds of hours on a large computer, we can perhaps perform an energy-calculation of a molecule not very much larger than benzene and the accuracy is not necessarily satisfactory. The ground state dissociation energies of many diatomic molecules calculated by the Hartree-Fock method have been shown to be one quarter to one half of their experimental values. For the fluorine molecule the Hartree-Fock calculations do not predict any binding energy (-1.37 ev) whereas the experimental binding energy is 1.68 ev.[2] Wahl[2a] pointed out that there might be two reasons for not getting binding in fluorine. First,

for many molecular systems the molecular orbital wave function does not exhibit the proper dissociation behavior (i.e. it goes into neutral and ionic atomic states). Second, when bonding occurs the correlation energy of the molecule increases, and this increase tends to raise the electronic energy of the molecule. Using an optimized configuration function, Das and Wahl[2b] have obtained some binding energy (0.5 ev) for the fluorine molecule.

As ab initio calculations are not possible for very large molecules organic and inorganic chemists use semi-empirical quantum chemical methods to interpret and correlate experimental results. The basic merit of the semi-empirical approach lies in its practical applicability to large molecular systems. Generally speaking the semi-empirical methods have been reasonably successful. A review of their development will be presented in order to set the stage for a new formulation of an all-valence-electron semi-empirical method to be described in the present work.

Hund and Mulliken introduced the molecular orbital (M.O.) theory as early as 1928. In 1931 Hückel[3] applied the theory in its simple form to conjugated hydrocarbons. Later the theory was developed by Lennard-Jones,[4] Coulson and Longuet-Higgins[5] and others, and it has been successfully used to study the properties of

conjugated molecules, olefins and aromatic compounds.

In Hückel π-electron theory the first basic assumption is that interactions between π-electron and other electrons are comparatively small. π-electrons are assumed to be well separated from other electrons. The second assumption is that the one-electron Hamiltonian is represented by

$$H(1,2,\ldots,n) = \sum_{i=1} h_{eff}(i) \qquad \text{(I-1)}$$

which means that the electrons are supposed to move independently in a potential field in which electron interactions are accounted for in an averaged form. Here the core is formed by all the nuclei and all the electrons other than the π-electrons. Each π-electron is treated as though it were in the averaged potential field due to the core and other π-electrons.

According to the assumed Hamiltonian (I-1) the many-body Schrödinger equation can be separated into a set of one-electron equations and the total wave function can be expressed as a simple product of MO's ψ_i

$$\Psi(1,2,\ldots,n) = \prod_{i=1}^{n} \psi_i(i) \qquad \text{(I-2)}$$

Each molecular orbital is an eigenfunction of h_{eff}.

$$h_{eff}\,\psi_i = \varepsilon_i \psi_i \qquad \text{(I-3)}$$

The total π-electron energy is given by

$$E_\pi = \sum_i n_i \varepsilon_i \qquad \text{(I-4)}$$

where n_i is the occupation number of orbital ψ_i and can be equal to 0, 1, or 2.

The third basic assumption is that the MO's are expressed as linear combinations of atomic orbitals, i.e.

$$\psi_i = \sum_\mu C_{\mu i} \chi_\mu \qquad \text{(I-5)}$$

where the χ_μ's are the $2p_\pi$ atomic orbitals. The orbital energies and the coefficients $C_{\mu i}$ can be obtained by solving the secular equation

$$\sum_\mu (h_{\mu\nu} - \varepsilon S_{\mu\nu}) C_{\nu i} = 0 \qquad \text{(I-6)}$$

where the matrix components are

$$h_{\mu\mu} = \langle \chi_\mu | h_{eff} | \chi_\mu \rangle = \alpha_\mu \qquad \text{(I-7)}$$

$$h_{\mu\nu} = \langle \chi_\mu | h_{eff} | \chi_\nu \rangle = \beta_{\mu\nu} \qquad \text{(I-8)}$$

and

$$S_{\mu\nu} = \langle \chi_\mu | \chi_\nu \rangle \qquad \text{(I-9)}$$

The secular equations are simplified by means of the following approximations:

(1) All the coulomb integrals, α_μ, are assumed to be equal, i.e. $\alpha_1 = \alpha_2 = \ldots = \alpha$.

(2) The resonance integrals $\beta_{\mu\nu}$ are assumed to be non-zero if atom μ is bonded to atom ν, represented by $\mu \rightarrow \nu$. $\beta_{\mu\nu}$ is set equal to zero when atom μ is not bonded to atom ν. This approximation is known as the neglect of non-neighbour interactions.

(3) All the resonance integrals for bonded carbon atoms have the same magnitude and are represented by the symbol β, i.e., $\beta_{\mu\nu} = \beta \neq 0$ if $\mu \rightarrow \nu$.

(4) All the overlap integrals $S_{\mu\nu}$ for $\mu \neq \nu$ are neglected. For normalized atomic orbitals $S_{\mu\mu} = 1$, i.e., it is assumed that $S_{\mu\nu} = \delta_{\mu\nu}$ where $\delta_{\mu\nu}$ is the Kronecker delta. This approximation is known as the neglect of overlap integrals or the zero overlap approximation.

Coulson and Longuet-Higgins[5a] have shown that the total π-energy is related to π-electron charge density and bond order and may be expressed by

$$E = \sum_\mu q_\mu \alpha + 2\sum_{\mu\nu} p_{\mu\nu}\beta \qquad \text{(I-10)}$$

where q_μ and $p_{\mu\nu}$ are respectively charge density and bond order defined by

$$q_\mu = 2\sum_i c_{\mu i}^2 \qquad \text{(I-11)}$$

$$p_{\mu\nu} = 2 \sum_{i} c_{\mu i} c_{\nu i} \qquad \text{(I-12)}$$

The Hückel procedure is very simple and ground state properties for conjugated molecules, especially alternant hydrocarbons, can be predicted well. But it does not give good results for ionization potentials, electron affinities and excitation energies. The defect in this simple theory is that it does not give a precise definition of the one-electron Hamiltonian. Electron interaction is also not explicitly taken into account. As a result there is no energy difference between a singlet and a triplet state.

The next attempt to develop the π-electron theory was made by Goeppert-Mayer and Sklar.[6] Electron interaction was taken into account and the LCAO approximation [equation (I-5)] was employed. The wave functions were made antisymmetrical with respect to exchange of electrons by multiplying them by appropriate spin functions. The Hamiltonian is represented by the equation

$$H(1,2,\ldots,n) = \sum_{\mu} H_{core}(\mu) + \sum_{\mu<\nu} \frac{e^2}{r_{\mu\nu}} \qquad \text{(I-13)}$$

where $\frac{e^2}{r_{\mu\nu}}$ is the repulsion between π electrons μ and ν and $H_{core}(\mu)$ is the kinetic energy operator for electron μ and its potential energy operator in the field of the core. Thus

$$H_{core}(\mu) = T(\mu) + U_{core}(\mu) \qquad \text{(I-14)}$$

or

$$H_{core}(\mu) = T(\mu) + U_p(\mu) + \sum_{q \neq p} U_q(\mu) + \sum_r U_r^*(\mu) \qquad \text{(I-15)}$$

where T is the kinetic energy operator, U_p is the potential energy operator due to the p^{th} carbon center in the core and U_r is the potential energy operator due to the r^{th} hydrogen atom in the core; * signifies a potential due to a neutral atom. The atomic orbitals χ_p are now taken to be atomic eigenfunctions of the operator $(T + U_p)$ such that

$$[T(\mu) + U_p(\mu)]\ \chi_p(\mu) = I_p \chi_p(\mu) \qquad \text{(I-16)}$$

where I_p is an appropriate valence state ionization potential. The potential energy operators U_q may be expressed as

$$U_q(\mu) = U_q^*(\mu) - \int \chi_q(\nu)\ \chi_q(\nu)\ \frac{e^2}{r_{\mu\nu}}\ dv(\nu) \qquad \text{(I-17)}$$

According to the Goeppert-Mayer and Sklar formulation α_p is given by

$$\alpha_p = \int \chi_p(\mu)\ H_{core}(\mu)\ \chi_p(\mu)\ dv$$

$$= I_p - \sum_{q \neq p} [(pp|qq) + (q{:}pp)] + \sum_r (r{:}pp) \qquad \text{(I-18)}$$

where $(pp|qq)$ is the coulomb repulsion integral between

atomic orbitals χ_p and χ_q, (q:pp) and (r:pp) are coulomb penetration integrals between χ_p and neutral atom q and r. Thus

$$(q:pp) = -\int U_q^* (\mu)\ \chi_p(\mu)\ \chi_p(\mu)\ d\nu \qquad \text{(I-19)}$$

In this method complicated atomic two center integrals were calculated and evaluated explicitly. Only the integrals involving overlap densities between non-nearest neighbours were neglected. They applied their method to benzene. The method does not work very well. The singlet-triplet splittings appear but are too big. The integrals are very difficult to compute. Moreover, the results of a calculation on the oxygen molecule using this method are in remarkable discord with experiment.[7] Thus in order to develop a workable and useful π-electron theory the following points should be considered:

(1) π-electrons should be treated separately from other electrons.

(2) The orbital wave functions should be made up from π-electron orbitals on the individual atoms.

(3) π-electron repulsions should be considered.

(4) The treatment of π-electron repulsions should be simplified.

(5) The theory must have some provision to use atomic data.

(6) Empirical elements should be included as adjustable parameters.

The Hückel method satisfies 1, 2, and 6 and Goeppert-Mayer and Sklar method fails in 4,5, and 6. In 1953 a theory[8,9] was put forward in which all of these characteristics are present. The theory presented by Pariser-Parr[8] incorporates empirical elements in the antisymmetric molecular orbital configuration interaction (ASMOCI) method. Pople[9] has introduced a set of simplifying approximations closely related to the Pariser-Parr approximation. Sometimes the Pariser-Parr method and the Pople method are combined as the Pariser-Parr-Pople (P-P-P) method. The main features of the original theory are similar to those of the Goeppert-Mayer and Sklar method with the exception of the way some types of integrals are evaluated. The one-center core integrals are calculated in the same way as in the Goeppert-Mayer and Sklar method [equation (I-18)]. The integrals S_{pq} and β_{pq} are treated in the same way as in the Hückel method, i.e.

$$S_{pq} = \delta_{pq} \tag{I-20}$$

and

$$\beta_{pq}^{core} = \begin{cases} \text{a parameter when atoms p and q are bonded} \\ 0 \text{ otherwise} \end{cases} \tag{I-21}$$

In order to reduce the number of electronic repulsion integrals the zero differential overlap (ZDO) approximation[10] was made, i.e.

$$\chi_p(1)\ \chi_q(1)\ dv(1) = 0 \text{ for } p \neq q \qquad \text{(I-22)}$$

This eliminates all electron repulsion integrals except those of the type (pp|qq) or (pp|pp) where the notation (pq|rs) means

$$(pq|rs) = \int \chi_p(1)\ \chi_q(1)\ \frac{e^2}{r_{12}}\ \chi_r(2)\ \chi_s(2)\ dv_1 dv_2 \qquad \text{(I-23)}$$

Here the integrals are formulated in terms of real functions. In other words, in the ZDO approximation, the hybrid (pp|pq), exchange (pq|pq) and many-center (pq|rs) integrals, all vanish.

The coulomb integrals, γ_{pq}, are computed theoretically or semi-empirically subject to the condition

$$\gamma_{pq} = \frac{1}{R} \qquad \text{(I-24)}$$

for large R (= $|\vec{r}_p - \vec{r}_q|$). When p = q one can use the formula of Pariser[11]

$$\gamma_{pp} = I - A \qquad \text{(I-25)}$$

where I is the ionization potential and A is the orbital electron affinity.

Mulliken[12] has estimated I and A to be 11.22

ev and 0.69 ev respectively for carbon atom. Thus $(pp|pp) = 10.53$ ev. Using Slater orbitals with the orbital exponent $Z = 3.18$, an explicit theoretical formula[13] gives

$$(pp|pp) = 16.93 \text{ ev} \qquad \text{(I-26)}$$

The applicability of the ZDO approximation can be justified by assuming that orthogonalized atomic orbitals (OAO) are used as the basis functions instead of overlapping atomic orbitals.

The orthogonalization of a non-orthogonal complete set of functions can be done in many ways. One of them was proposed by Löwdin[14] and according to him OAOs can be represented by

$$\lambda = \chi S^{-1/2} \qquad \text{(I-27)}$$

where λ and χ are row matrices and S is the square matrix of overlap integrals in the nonorthogonal basis. When the orbital basis is transformed according to equation (I-27) the matrix representation of any one-electron operator M will also be transformed according to the equation

$$\lambda_M = S^{-1/2} M S^{-1/2} \qquad \text{(I-28)}$$

where $^{\lambda}M$ refers to the matrix representation of the operator in the orthogonalized atomic orbital basis, $\{\lambda\}$ and matrices without superscripts refer to the matrix representation of the operator in the atomic orbital basis, $\{\chi\}$. It has been shown by Inga-Fischer-Hjalmars[15] that transformation (I-27) to (I-28) will be approximately equal to ZDO approximation.

There are many choices which can be made for expanding molecular orbitals. These are (a) Slater-type orbital, (b) distorted atomic orbital, (c) combinations of (a) and (b).

In the Pariser-Parr-Pople method one assumes the second choice of the orbital where the explicit form of the distorted atomic orbitals does not need to be specified. Here all the parameters are used as empirical quantities except coulomb repulsion integrals. This procedure is justified because the operator involved is simple and the asymptotic form of the interaction is well understood.

In the Pariser-Parr-Pople method both the ZDO approximation and the determination of certain integrals in an empirical way have been included. It has been shown that the ZDO approximation can only be applicable to orthonormalized bases. As a result the local character of various integrals will be destroyed. Hence the trans-

ference of numerical values from one molecule to another will be prohibited. However, Inga Fischer-Hjalmars[15] has shown that the pertinent integrals are independent of the surroundings.

Although the refined form of π-electron theory explains many of the properties of conjugated and aromatic systems it still cannot explain many chemical properties such as transition-state mechanisms in chemical reactions, steric hindrance and ring strain, etc. Moreover, the HMO and P-P-P methods were developed to study only planar conjugated molecules. Attempts have been made to use these methods to study non-planar molecules with σ electrons but they are of limited success. An improved theory is needed in which calculations should be based on all valence electrons. One of the first successful attempts was made by Hoffmann[16] who attacked the problem of treating all valence electrons in a quantitative manner with the application of the HMO method. In his method known as Extended Hückel Theory (EHT), all valence electrons are treated explicitly, all overlap integrals are calculated, only 1s electrons of carbon and heteroatoms are in the core and like the HMO method the Hamiltonian remains undefined. The secular equations and equations for orbital coefficients are given by the following equations:

$$|H_{\mu\nu} - ES_{\mu\nu}| = 0 \qquad \text{(I-29)}$$

$$\sum_{\nu}(H_{\mu\nu} - E_j S_{\mu\nu})\, C_{\nu j} = 0 \qquad \text{(I-30)}$$

The summation is over all valence shell atomic orbitals. The matrix elements $H_{\mu\nu}$ are defined by

$$H_{\mu\nu} = \int \chi_{\mu} \quad H \quad \chi_{\nu}\, dv \qquad \text{(I-31)}$$

The Hamiltonian H represents the energy of electrons in the field of a core made up of nuclei, inner shell electrons and the valence electrons. The diagonal elements are determined semi-empirically and off-diagonal elements are estimated by the Mulliken[12] formula. Thus

$$H^{eff}_{\mu\mu} = \alpha_{\mu} = I \qquad \text{(I-32)}$$

and

$$H^{eff}_{\mu\nu} = \frac{1}{2} K\, (\alpha_{\mu} + \alpha_{\nu}) S_{\mu\nu} \qquad \text{(I-33)}$$

where K is taken to be 1.75. Off-diagonal elements include all pairs of atomic orbitals. The total energy of the molecule is given by

$$E_{total} = \sum_{j}^{occ} E_j = \sum_{\mu} N_{\mu\mu} + (K - 1)(N_{\mu\mu} - P_{\mu\mu})\alpha_{\mu} \qquad \text{(I-34)}$$

where $N_{\mu\mu} = \sum_{\nu} P_{\mu\nu}\, S_{\mu\nu}$ is the gross atomic population.[12]

EHT is not free from criticisms which are applicable to HMO theory. It does not predict the correct heat of atomization and in many cases the charge density is far from reality. The failure of EHT led to the development of other sophisticated all-valence-electron methods in which π-σ interaction has been taken into account. Among these methods CNDO (complete neglect of differential overlap) is the first theory proposed by Pople *et al.*[17] In 1967 Pople and coworkers[18] also introduced the INDO (Intermediate neglect of differential overlap) method and this was followed by Dewar and Klopman's[19] partial neglect of differential overlap (PNDO) approach. In quick succession many other methods have been developed in this line in which the choice of parameters or method of parametrization is different from each other. As our work deals with all valence electrons, we shall discuss the methods in detail in Chapter III.

Chapter II

SCF THEORY AND ITS DEVELOPMENT FOR π-MOLECULAR SYSTEM

In order to discuss the all-valence-electron semi-empirical SCF theory, it appears most profitable to first outline the formulation of the SCF MO method by Roothaan[20] and its application by Pariser-Parr[8] and by Pople[9] using various approximations which are in the area of semi-empirical choices for the integrals.

Hartree-Fock-Roothaan Method:

The central problem in the elucidation of the electronic structure of N electron systems in a stationary state by wave-mechanical means is the solution of Schrödinger equation

$$H\Psi_i = E\Psi_i \qquad \text{(II-1)}$$

where H is the total Hamiltonian operator of the system, Ψ is the wave function and E the energy eigenvalue. The wave function depends on the electronic coordinates each consisting of a space coordinate and a spin coordinate. It is well known that the solution of equation (II-1)

involves considerable difficulties. In order to obtain a good approximate solution of equation (II-1) the variation principle is to be used. Expressing the total wave function for N electrons as an antisymmetrized product (AP)

$$\Psi = (N!)^{-\frac{1}{2}} \begin{vmatrix} \psi_1(1) & \psi_2(1) & \ldots & \psi_N(1) \\ \vdots & & & \vdots \\ \psi_1(N) & \ldots & & \psi_N(N) \end{vmatrix} \qquad \text{(II-2)}$$

For closed shell systems the molecular spin orbitals (MSO) are given by

$$\psi_{2i-1} = \phi_i\alpha \qquad \psi_{2i} = \phi_i\beta \qquad \text{(II-3)}$$

With 2n electrons the antisymmetrized product may then be written as

$$\Psi = [(2n)!]^{-\frac{1}{2}} \left| \phi_1(1)\alpha(1)\phi_1(2)\beta(2) \ldots \right.$$

$$\left. \ldots \phi_n(2n-1)\alpha(2n-1)\ \phi_n(2n)\beta(2n) \right| \qquad \text{(II-4)}$$

The MSO's are assumed to be orthonormal,

$$\int \bar{\psi}_i \psi_j d\tau = \delta_{ij} \qquad \text{(II-5)}$$

An important implication of the above equation is that the AP given by equation (II-2) is normalized i.e.

$$\int \bar{\Psi}\,\Psi \, d\tau = 1 \qquad \text{(II-6)}$$

The electronic energy for an electronic state represented by the normalized wave function is given by

$$E = \int \bar{\Psi}\, H \Psi \, d\tau \qquad \text{(II-7)}$$

where the total Hamiltonian, defined earlier by equation (I-13), is in a.u.

$$H = \sum_{\mu} H(\mu) + \frac{1}{2} \sum_{\mu \neq \nu} \frac{1}{r_{\mu\nu}}$$

$$\text{with} \qquad H(\mu) = -\frac{1}{2} \nabla^2 - \sum_{a} \frac{Z_a}{r_{a\mu}} \qquad \text{(II-8)}$$

Substituting the wave function equation (II-4) into the energy expression (II-7) and performing the necessary algebra, we find the energy of a closed shell AP to be

$$E = 2\sum_{i} H_i + \sum_{ij} (2J_{ij} - K_{ij}) \qquad \text{(II-9)}$$

where the nuclear field orbital energies H_i, coulomb integrals J_{ij} and exchange integrals K_{ij} are defined by

$$H_i = \bar{H}_i = \int \bar{\phi}_i(\mu)\ H\ (\mu)\ \phi_i(\mu) dv_\mu \qquad \text{(II-10)}$$

$$\left.\begin{aligned} J_{ij}=J_{ji}=\bar{J}_{ij}=\bar{J}_{ji}&=\iint \bar{\phi}_i(\mu)\bar{\phi}_j(\nu)\left(\frac{1}{r_{\mu\nu}}\right)\phi_i(\mu)\phi_j(\nu)dv_\mu dv_\nu \\ K_{ij}=K_{ji}=\bar{K}_{ij}=\bar{K}_{ji}&=\iint \bar{\phi}_i(\mu)\bar{\phi}_j(\nu)\left(\frac{1}{r_{\mu\nu}}\right)\phi_j(\mu)\phi_i(\nu)dv_\mu dv_\nu \end{aligned}\right\} \qquad \text{(II-11)}$$

From equation (II-11) it is clear that

$$J_{ii} = K_{ii} \qquad \text{(II-12)}$$

It is useful to define a coulomb operator J_i and an exchange operator K_i by the following equations

$$\left.\begin{aligned} J_i(\mu)\phi(\mu) &= \left(\int \frac{\bar{\phi}_i(\nu)\ \phi_i(\nu)}{r_{\mu\nu}}\, dv_\nu\right)\phi(\mu) \\ K_i(\mu)\ \phi(\mu) &= \left(\int \frac{\bar{\phi}_i(\nu)\ \phi(\nu)}{r_{\mu\nu}}\, dv_\nu\right)\phi_i(\mu) \end{aligned}\right\} \qquad \text{(II-13)}$$

These operators are hermitian and linear. J_i is the operator expressing the potential due to an electron distributed in space with the density $|\phi_i|^2$. However K_i has no classical analog.

In order to obtain the AP for which the energy of the system reaches a minimum, the expression (II-9) is to be minimized by varying the MO's within the limits that they form an orthonormal set such that

$$\int \bar{\phi}_i \phi_j dv = \delta_{ij} \qquad \text{(II-14)}$$

When each MO ϕ_i varied by an infinitesimal amount $\delta\phi_i$ the energy is also varied by an amount δE. The condition for E to reach a minimum is that $\delta E = 0$ for any infinitesimal variation of the ϕ_i's. This condition is given by

$$\left.\begin{aligned} \left\{ H + \sum_j (2J_j - K_j) \right\} \phi_i &= \sum_j \phi_j \, \varepsilon_{ji} \\ \left\{ \bar{H} + \sum_j (2\bar{J}_j - \bar{K}_j) \right\} \bar{\phi}_i &= \sum_j \bar{\phi}_j \, \varepsilon_{ij} \end{aligned}\right\} \qquad \text{(II-15)}$$

where ε_{ij} are Lagrangian multipliers. It can be shown that Lagrangian multipliers are the elements of a hermitian matrix. As a result the two equations (II-15) are equivalent. The equations are known as Hartree-Fock equations proposed simultaneously and independently by Fock[21] and Slater[22].

We now define the Hartree-Fock operator

$$F = H + \sum_j (2J_j - K_j) \qquad \text{(II-16)}$$

For the best MO's to satisfy the equation (II-15) we can write

$$F\phi_i = \sum_j \phi_j \varepsilon_{ji} \qquad \text{(II-17)}$$

It is known that without changing the physical content of the total wave function (II-2) we may cast the equation (II-17) into the following form

$$F\phi_i = \varepsilon_i \phi_i \qquad \text{(II-18)}$$

The set of equations (II-18) is most commonly known as Hartree-Fock equation.

The general procedure for solution of the Hartree-Fock equations is to choose a set of trial solutions, from which coulomb and exchange operators are formed and the Hartree-Fock Hamiltonian operator is calculated. Then the equation (II-18) is solved for n lowest eigenvalues and the resulting ϕ_i's are compared with the assumed ones and a new set of ϕ_i's is chosen from the knowledge of this comparison. This process is then repeated until the energy value of the calculated and assumed ϕ_i's agree.

This method for solving the Hartree-Fock equation is known as the Hartree-Fock self consistent field (SCF) method.

Although the Hartree-Fock method gives a useful approximate solution to the Schrödinger equation, it has been used in its original form of integro-differential equations almost exclusively for atoms. For molecular systems which lack spherical symmetry, it is almost impossible to solve the equation effectively. In order to overcome this difficulty Roothaan[20] has developed a method to obtain solutions to Hartree-Fock equations avoiding numerical integrations.

Let $\{\chi_\mu\}$ represent a complete basis set of functions which are normalized although they may not be orthogonal in general. Each Hartree-Fock orbital can be expanded in terms of their basis set

$$\phi_i = \sum_\mu \chi_\mu C_{\mu i} \quad = \quad \chi\, C_i \quad \ldots\ldots \qquad \text{(II-19)}$$

where C_i is the column matrix of m rows such as

$$C_i = \begin{bmatrix} C_{1i} \\ C_{2i} \\ \vdots \\ C_{mi} \end{bmatrix} \quad \text{and} \quad \chi = (\chi_1\ \chi_2\ \ldots\ldots \chi_m)$$

If $\{\chi_\mu\}$ constitute a complete basis set then $\{\phi_i\}$ are given exactly. However in practice the expansion is truncated to m finite members of the basis set. The condition for constructing n linearly independent solutions is that $m \geq n$.

If $\{\phi_i\}$ form an orthogonal set then it requires that

$$\sum_{\mu,\nu} C_{\mu i}^{*} S_{\mu\nu} C_{\nu j} = \delta_{ij} \qquad \text{(II-20)}$$

where $\delta_{\mu\nu}$ is the Kronecker delta and S_{ij} is the overlap integral for atomic functions defined by

$$S_{ij} = \int \bar{\phi}_i \phi_j \, dv$$

$$= \sum_{\mu} \sum_{\nu} \int \bar{\chi}_\mu \chi_\nu \, dv \, C_{\mu i}^{*} C_{\nu j}$$

$$= C_i^{*} S C_j = \delta_{ij} \qquad \text{(II-21)}$$

where

$$C_i^{*} = (\bar{C}_{1i} \bar{C}_{2i} \ldots\ldots \bar{C}_{mi})$$

and S is a hermitian matrix the elements of which are overlap integrals represented by the equation (II-21) and diagonal elements are unity.

Let us define the following matrix elements and matrices

$$H_i = C_i^* H C_i \qquad \text{(II-22)}$$

$$\left.\begin{aligned} J_{ij} &= C_i^* J_j C_i = C_j^* J_i C_j \\ K_{ij} &= C_i^* K_j C_i = C_j^* K_i C_j \end{aligned}\right\} \qquad \text{(II-23)}$$

In order to obtain the best LCAOMO's a variational treatment is to be carried out. When the vector C_i is varied by an infinitesimal amount δC_i, the coefficients $C_{\mu i}$ are also varied by a small amount $\delta C_{\mu i}$. The condition for the energy to be a minimum is $\delta E = 0$. The Euler equation for this variational treatment assumes the following form

$$F C_i = \sum_j S C_j \varepsilon_{ji} \qquad \text{(II-24)}$$

or in a more compact notation.

$$F \mathbf{C} = S \mathbf{C} \varepsilon \qquad \text{(II-25)}$$

The equation is known as Roothaan's equation. If ε represents a diagonal matrix with real diagonal elements ε_i the equation (II-25) takes the form

$$F C_i = \varepsilon_i S C_i \qquad \text{(II-26)}$$

The non-trivial solutions of equation (II-25) are obtained by solving for m roots of the secular determinant

$$\det |F - \varepsilon S| = 0 \qquad \text{(II-27)}$$

Since the matrix F depends on $\{C_i\}$ the secular equations are non-linear and should be solved by iterative techniques. This can be done as follows. As a first approximation some matrix $\mathbf{C}^{(1)}$ is assumed and utilized to construct $F^{(1)}$; then equation (II-27) is solved to obtain a first improved matrix $\mathbf{C}^{(2)}$. This process is continued until the matrices between two successive iterations agree within a specified limit when the solutions are said to be self-consistent with respect to elements of matrix $\mathbf{C}$. Since the basis orbitals $\{\chi_\mu\}$ are not varied this method does not give true Hartree-Fock solutions unless the basis used is large. The lowest n roots correspond to those occupied by 2n electrons describing the ground state of the atom.

The rest of the solutions are known as virtual orbitals and may be used to construct excited state configurations. The energy can be improved by the configuration interaction method.

Ab initio Hartree-Fock-Roothaan molecular calculations are limited at present to moderately large molecular systems. The difficulty is in the evaluation of the integrals of the type $(ij|kl)$ because the number of such integrals is very large and increases roughly as the fourth power of the number of functions of the basis set. Moreover, the determination of these integrals presents technical difficulties for functions which are orbitals of three or four different atoms. In addition, it is seen that the results of such calculations are frequently not in good agreement with experiment. Hence it seems that it is desirable to have methods which give better agreement with experiment and which are simple enough to permit extension of our calculations to larger molecules.

Pariser-Parr-Pople Method:

The essence of the Pariser-Parr-Pople (P-P-P) method for obtaining the wave functions and energies of a given π system is as follows:

(a) The Hamiltonian operator for the π electrons of a given molecule may be represented by equation (I-13).

(b) The molecular orbitals may be expressed as linear combinations of atomic orbitals as in equation (I-5).

The energy of the system containing π - electrons can be determined by using the Hartree-Fock-Roothaan SCF method. For this purpose we need to know the value of the electron interaction integrals. The application of the ZDO assumption reduces the number of integrals from the order of n^4 to n^2 where n is the number of π-electrons of the system. The matrix elements are represented by the formula

$$F_{\mu\mu} = \alpha_\mu + \frac{1}{2} P_{\mu\mu} \gamma_{\mu\mu} + \sum_\nu P_{\nu\nu} \gamma_{\mu\nu} \qquad \text{(II-28)}$$

$$F_{\mu\nu} = \beta_{\mu\nu} - \frac{1}{2} P_{\mu\nu} \gamma_{\mu\nu} \qquad (\mu \neq \nu) \qquad \text{(II-29)}$$

where $\alpha_\mu = \left(\chi_\mu(1) | H_{core}(1) | \chi_\mu(1)\right)$ (II-30)

$$\beta_{\mu\nu} = (\chi_\mu(1) | H_{core}(1) | \chi_\nu(1)) \qquad \text{(II-31)}$$

$P_{\mu\nu}$ is the bond-order matrix and $\gamma_{\mu\nu}$ is the coulomb repulsion integral.

Now α_μ is the energy (kinetic and potential) of an electron in the orbital χ_μ in the framework field. If we write the potential energy term as $v=v_1+v_2.....$ we have

$$\alpha_\mu = (\chi_\mu|-\tfrac{1}{2}\nabla^2+v_\mu|\chi_\mu)+\sum_{\nu\neq\mu}(\chi_\mu|v_\nu|\chi_\mu)$$

$$= U_\mu + \sum_{\nu\neq\mu}(\chi_\mu|v_\nu|\chi_\mu) \qquad \text{(II-32)}$$

and $$\beta_{\mu\nu} = (\chi_\mu| -\tfrac{1}{2}\nabla^2+v_\mu+v_\nu|\chi_\nu)+\sum_{p\neq\mu,\nu}(\chi_\mu|v_p|\chi_\nu) \qquad \text{(II-33)}$$

Thus

$$F_{\mu\mu} = U_\mu+\tfrac{1}{2}P_{\mu\mu}\gamma_{\mu\mu}+\sum_\nu P_{\nu\nu}\gamma_{\mu\nu}+\sum_{\nu\neq\mu}(\chi_\mu|v_\nu|\chi_\mu) \qquad \text{(II-34)}$$

U_μ, which is regarded as an empirical parameter, can be taken as constant for a given atom. If χ_μ is an eigenfunction of the isolated atom then U_μ is the energy of an electron in the orbital χ_μ and this may be taken to be equal to the valence state ionization potential I_μ of the atom i.e. the ionization potential of an atom in its proper hybridised state in the molecule. For a given pair of atoms and given bond length the first term in $\beta_{\mu\nu}$ can be taken as constant. Since the potential due to a distant nucleus having unit charge is equal and

opposite in sign to the potential due to a distant electron density χ_p^2, it follows that

$$(\chi_\mu|v_p|\chi_\nu) = -Z_p\ (\mu\nu|pp) \qquad \text{(II-35)}$$

where Z_p is the charge on the core at atom P.

According to the zero overlap approximation two electron integrals of the type in equation (II-35) are equal to zero. Hence the sum over distant cores in $\beta_{\mu\nu}$ can be neglected. Thus $\beta_{\mu\nu}$ can be taken as an empirical parameter and is constant in a given type of bond; $\beta_{\mu\nu}$ is assumed to be zero for non-bonded atoms as in Hückel theory. But it should be noted that the β value used in Hückel theory for a particular type of bond is not the same as that needed in P-P-P method because in Hückel theory β compensates the neglect of all electron repulsion terms.

Adopting the approximation (II-35) for the case $\mu=\nu$, we have

$$\alpha_\mu = I_\mu - \sum_{p\neq\mu} Z_p\ \gamma_{\mu p} \qquad \text{(II-36)}$$

If we use the value of α_μ in equation (II-36), $F_{\mu\mu}$ takes the form

$$F_{\mu\mu} = I_\mu + \frac{1}{2} P_{\mu\mu}\gamma_{\mu\mu} + \sum_\nu (P_{\nu\nu} - Z_\nu)\gamma_{\mu\nu} \qquad \text{(II-37)}$$

In the ZDO approximation Pople used expression (II-29) and (II-37) for the construction of SCF molecular orbitals.

The ZDO assumptions suggested by Pariser and Parr[8] and by Pople[9] may be summarized below:

$$(\mu|S|\nu) = \delta_{\mu\nu} \qquad \text{(II-38)}$$

$$(\mu|H_{core}|\mu) \neq 0 \qquad \text{(II-39)}$$

$$(\mu|H_{core}|\nu) \neq 0 \text{ (where } \mu \text{ and } \nu \text{ are neighbors)} \qquad \text{(II-40)}$$

$$(\mu|H_{core}|\nu) = 0 \text{ when } \mu \text{ and } \nu \text{ are non-neighbors} \qquad \text{(II-41)}$$

$$(\mu\nu|k\eta) = \delta_{\mu\nu}\delta_{k\eta}\gamma_{\mu\eta} \qquad \text{(II-42)}$$

where

$$\gamma_{\mu\eta} = \int |\chi_\mu(1)|^2 \left(\frac{1}{r_{12}}\right) |\chi_\eta(2)|^2 \, dv_1 \, dv_2$$

The ZDO relation of equation (II-42) was suggested by Parr previous to the assumption (II-38) to (II-41).

These equations (II-34) to (II-41) were introduced by Pariser and Parr[8] and Pople[9] as useful simplifications. But Fischer-Hjalmars[15] has shown that these approximations were largely justified if the basic atomic orbitals are taken to be Löwdin orthogonalized atomic orbital (OAO) instead of Slater orbitals.

In π-electron theory the core resonance integral, β, is treated as an empirical parameter and is determined to fit an experimental property. For example in recent years there are two groups of β values for a C-C bond (1.40 A°) found in the literature. One, higher value -2.39 ev[8] is used for the prediction of spectral transitions and the other lower value (-1.75 ev)[23] utilized to predict the ground state properties such as heat of atomization, resonance energy and bond energy, etc.

There are several methods for evaluation of resonance integrals

(a) To fit the lowest singlet-singlet transition energy.

(b) Chung and Dewar[23] and Lo and Whitehead[24] evaluated the integral using a hypothetical thermocycle.

(c) In the β variable method as proposed by Yamaguchi et al[25] two center core integrals $\beta_{\mu\nu}$, the bond length $r_{\mu\nu}$ and the two-center repulsion integrals $\gamma_{\mu\nu}$ between

neighboring atoms are adjusted at each iteration according to the following equations until the self-consistency was achieved.

$$\left.\begin{aligned} r_{\mu\nu}\ (A^\circ) &= 1.520-0.186P_{\mu\nu} \\ \beta_{\mu\nu} &= \beta_o \exp\left[a\ (r_o-r_{\mu\nu})\right] \end{aligned}\right\} \qquad \text{(II-43)}$$

r_o is the C-C distance for benzene, a=1.7 $A^{\circ -1}$ and β_o is the resonance integral for C-C bond in benzene.

(d) Resonance integrals may be related to overlap integrals by the equation

$$\beta = -kS \qquad \text{(II-44)}$$

where S is the overlap integral evaluated using Slater-Zener orbitals (Z=3.18) and k is a proportionality constant; for carbon-carbon the value is taken to be 6.927[26].

Two center two electron integrals $(\mu\mu|\nu\nu)$ are calculated in the following ways:

(a) By the charged sphere approximation[8].

(b) Pople method:

$$\left.\begin{aligned} (\mu\mu|\nu\nu) &= \frac{14.3968}{r_{ab}} \quad \text{where r is in } A^\circ \\ &= \frac{1}{r_{ab}} \quad \text{where r is in a.u} \end{aligned}\right\} \qquad \text{(II-45)}$$

(c) Method due to Mataga and Nishimoto[27]

$$(\mu\mu|\nu\nu) = \frac{14.3968}{a + r_{\mu\nu}} \quad \text{where r is in A°}$$

$$= \frac{1}{a + r_{\mu\nu}} \quad \text{where r is in a.u.} \qquad \text{(II-46)}$$

where

$$a = \frac{14.3968}{\frac{1}{2}(I_\nu - A_\nu) + \frac{1}{2}(I_\mu - A_\mu)} \text{ in A° or}$$

$$= \frac{1}{\frac{1}{2}(I_\nu - A_\nu) + \frac{1}{2}(I_\mu - A_\mu)} \text{ in a.u.} \qquad \text{(II-47)}$$

(d) Ohno's method[28]:

$$(\mu\mu|\nu\nu) = \frac{14.3968}{(r_{\mu\nu}^2 + a^2)^{1/2}} \quad \text{where r in A°}$$

$$= \frac{1}{(r_{\mu\nu}^2 + a^2)^{1/2}} \quad \text{where r in a.u} \qquad \text{(II-48)}$$

where a is defined as in equation (II-47). There are many other formulas for the evaluation of γ integrals but Mataga and Nishimoto's method[27] and Ohno's method[28] are most commonly used. It is seen that for the study of ground state properties of molecules Ohno's method is

better than Mataqa-Nishimoto's method whereas Mataga-Nishimoto's formula is superior in the context of CI studies.

It would be an interesting invention if we could construct a simple formula which would reproduce both Ohno's and Mataga-Nishimoto's values and also Roothaan's theoretical values of coulomb integrals as special cases. In the following we introduce such a formula which will be discussed in more detail in Chapter IV.

$$\left.\begin{aligned}(\mu\mu|\nu\nu) &= \frac{14.3968}{R+A} \quad \text{when R is in A°} \\ &= \frac{1}{R+A} \quad \text{when R is in a.u}\end{aligned}\right\} \qquad \text{(II-49)}$$

where

$$R = R_{\mu\nu} \text{ and } A = \frac{1}{a_\mu e^{\kappa_\mu R} + a_\nu e^{\kappa_\nu R}} \text{ in a.u.}$$

Chapter III

ALL-VALENCE-ELECTRON METHODS

The importance of molecular orbital calculations would be much increased if the methods which have been described in Chapter II were extended to all valence electrons instead of being restricted to the level of π-electrons only. Such an advance would permit not only a full treatment of σ and π electrons in planar molecules but would also allow the calculation of a large number of molecules where σ-π separation is not possible.

Since EHT is not free from disadvantages similar to the Hückel theory, a theory concerning all valence electrons is needed in which electron repulsions have been taken into account. In the following we would like to discuss some of the methods in which all valence electrons are included.

The CNDO Method:

The CNDO (complete neglect of differential overlap) method proposed by Pople et al[17] assumes that the product of orbitals $\chi_\mu \chi_\nu$ is always zero provided that

χ_μ and χ_ν are different. According to this approximation the overlap integrals $S_{\mu\nu}$ between any pair of different orbitals is zero except in $H_{\mu\nu}$ (II-6) and all integrals $(\mu\nu|\lambda\sigma)$ are zero unless $\mu=\nu$ and $\lambda=\sigma$. The integrals $(\mu\mu|\lambda\lambda)$ are written as $\gamma_{\mu\lambda}$ and are assumed to depend on the atoms A and B to which χ_μ and χ_λ belong and not on the type of orbitals. Thus all the various $\gamma_{\mu\lambda}$ between atoms A and B are approximated by Γ_{AB}. The Γ_{AB} are approximated in the original CNDO calculation by the purely theoretical values of the integral $(s_A s_A|s_B s_B)$ of the valence shell s orbitals.

With these approximations the Hartree-Fock matrix elements become

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\,\Gamma_{AA} + \sum_{B\neq A}(P_{BB}\Gamma_{AB} - \gamma_{AB}) \qquad \text{(III-1)}$$

$$F_{\mu\nu} = H_{\mu\nu} - \tfrac{1}{2}P_{\mu\nu}\,\Gamma_{AB} \quad (\mu\neq\nu) \qquad \text{(III-2)}$$

where the atomic orbitals χ_μ is connected on atom A and χ_ν on atom B. In deriving these equations Pople separated the core matrix elements $H_{\mu\mu}$. Thus

$$H_{\mu\mu} = (\chi_\mu|-\tfrac{1}{2}\nabla^2-V_A|\chi_\mu) - \sum_{A\neq B}(\chi_\mu|V_B|\chi_\mu)$$

$$= U_{\mu\mu} - \sum_{B\neq A} V_{AB} \qquad \text{(III-3)}$$

The diagonal elements $H_{\mu\mu}$ may be split up into two parts: the first term $U_{\mu\mu}$ is that part of the diagonal matrix elements involving the one-electron Hamiltonian containing only the core of its own atom and terms, V_{AB}, containing the interaction of the electron in χ_μ on atom A with the cores of other atoms B and is approximated by the relation $\int S_A^2 \frac{Z_B}{r_{AB}} dv$. The value of $U_{\mu\mu}$ is approximated from atomic spectroscopy. The $P_{\mu\nu}$ are the components of the charge density and bond order matrix

$$P_{\mu\nu} = 2 \sum_{m}^{occ} C_{m\mu} C_{m\nu} \qquad \text{(III-4)}$$

and $P_{\mu\mu}$, the total charge density on atom A is given by

$$P_{AA} = \sum_{\mu}^{A} P_{\mu\mu} \qquad \text{(III-5)}$$

Finally the off-diagonal elements $H_{\mu\nu}$ are taken as zero if χ_μ and χ_ν are on the same atom. But if χ_μ and χ_ν are on different atoms A and B, then

$$H_{\mu\nu} = \frac{1}{2} (\beta_A^\circ + \beta_B^\circ) S_{\mu\nu} \qquad \text{(III-6)}$$

where β_A° and β_B° are treated as adjustable parameters. Under the CNDO approximation the total energy of the molecule can be written as a sum of one- and two-atom terms.

$$E_{\text{Total}} = \sum_A E_A + \sum_{A<B} E_{AB} \qquad \text{(III-7)}$$

where

$$E_A = \sum_\mu^A P_{\mu\mu} U_{\mu\mu} + \frac{1}{2} \sum_\mu^A \sum_\nu^A (P_{\mu\mu} P_{\nu\nu} - \tfrac{1}{2} P_{\mu\nu}^2) \Gamma_{AA} \qquad \text{(III-8)}$$

and

$$E_{AB} = \sum_\mu^A \sum_\nu^B (2P_{\mu\nu} H_{\mu\nu} - \tfrac{1}{2} P_{\mu\nu}^2 \Gamma_{AB}) +$$

$$\left(\frac{Z_A Z_B}{R_{AB}} - P_{AA} V_{AB} - P_{BB} V_{BA} + P_{AA} P_{BB} \Gamma_{AB} \right) \qquad \text{(III-9)}$$

The interaction energy of the cores of atoms A and B is approximated by $Z_A Z_B R_{AB}^{-1}$ where Z_A and Z_B are the charges of the cores in units of +e.

One of the principal defects of CNDO/1 is that for diatomic molecules the calculated bond lengths are too short and binding energies are too large. This is due to the 'penetration' effect of electrons i.e. electrons in an orbital on one atom penetrate the shell of another giving rise to net attraction. Writing the equation (III-1) in the form

$$F_{\mu\mu} = U_{\mu\mu} + (P_{AA} - \tfrac{1}{2}P_{\mu\mu})\,\Gamma_{AA} + \sum_{B\neq A} (P_{BB} - Z_B)\Gamma_{AB}$$

$$+ \sum_{B\neq A} (Z_B \Gamma_{AB} - V_{AB}) \qquad \text{(III-10)}$$

the last term may be taken to be the contribution of penetration integrals to $F_{\mu\mu}$. In order to eliminate the above mentioned difficulties Pople and Segal[17] in a later paper modified the CNDO method known as CNDO/2. In this method the penetration terms in equation (III-9) are neglected by putting

$$V_{AB} = Z_B\,\Gamma_{AB} \qquad \text{(III-11)}$$

Although there is no complete justification for this, Pople and Segal[17] have suggested that neglect of overlap causes errors which are opposite in sign to the errors due to the neglect of penetration. Thus equation (III-11) corrects the CNDO/1 procedure in the right direction.

Another modification made in CNDO/2 is the method of estimating the local core matrix element $U_{\mu\mu}$. In CNDO/1 this was done by the relation

$$-I_{\mu} = U_{\mu\mu} + (Z_A - 1)\Gamma_{AA} \qquad \text{(III-12)}$$

where I_{μ} is the ionization potential in the appropriate average atomic state and orbital χ_{μ} belongs to atom A. An alternative procedure is to use atomic electron affinities,

$$-A_{\mu} = U_{\mu\mu} + Z_A \Gamma_{AA} \qquad \text{(III-13)}$$

In the CNDO/2 method the integral $U_{\mu\mu}$ is taken as the average of the ionization potential (I) and electron affinity (A).

Thus

$$-\frac{1}{2}(I_\mu+A_\mu) = U_{\mu\mu} + (Z_A-\frac{1}{2})\,\Gamma_{AA} \qquad \text{(III-14)}$$

and

$$U_{\mu\mu} = -\frac{1}{2}(I_\mu+A_\mu) - (Z_A-\frac{1}{2})\Gamma_{AA} \qquad \text{(III-15)}$$

Using equation (III-11) and (III-15) the basic equations for the Hartree-Fock matrix in the CNDO/2 formalism may be written as

$$F_{\mu\mu} = -\frac{1}{2}(I_\mu+A_\mu) + \left[(P_{AA}-Z_A) - \frac{1}{2}(P_{\mu\mu}-1)\right]\Gamma_{AA} + \sum_{B\neq A}(P_{BB}-Z_B)\,\Gamma_{AB} \qquad \text{(III-16)}$$

$$F_{\mu\nu} = \frac{1}{2}S_{\mu\nu}(\beta^\circ_A+\beta^\circ_B) - \frac{1}{2}P_{\mu\nu}\,\Gamma_{AB} \qquad \text{(III-17)}$$

Invariance Problem:

Pople and co-workers[17] pointed out that in a full Roothaan-SCF-MO treatment the two-center integrals are independent of the choice of axis but this is not so in simplified versions because these integrals are dependent on the choice of coordinate system and hybridization of the orbitals. Hence in the zero differential overlap methods the results of these integrals are required to be invariant to two types of transformations:

(1) Coordinate Invariance - invariance under rotation of the coordinate axis.

(2) Hybridization Invariance - invariance under rotation of the hybrid orbitals.

We shall discuss this invariance problem in more detail in Chapter V.

Evaluation of Integrals:

In the CNDO/1 method the overlap integrals are calculated theoretically. The electron repulsion integrals Γ_{AB} are calculated as the two-center coulomb integral involving valence s functions which have also been evaluated theoretically.

Defects of CNDO Level Methods:

Although the CNDO methods proposed by Pople et al[17] have been used successfully to calculate the properties of many species, they are not free from shortcomings. One of the serious defects of the parametrization of the theory is that the total energies of the occupied orbitals are uniformly too negative and the energies of the virtual orbitals are similarly displaced downwards. As a result the ionization potential and electron affinity are too large by several electron volts for all species studied. Moreover these methods do not give the correct energy or correct bond length relation although they are good for bond angles and charge densities[17]. The heats of formation calculated by CNDO in its original form were not in agreement with experimental results. As a result several authors tried to reparametrize CNDO methods in order to correlate the calculated and observed properties. Wiberg[29], by modifying Pople's parameters, was able to calculate structure (bond lengths and bond angles) and heats of atomization. He reduced the β proportionality constant and changed the ionization potential of the carbon atom. He also used a linear relationship between calculated

and experimental heats of atomization i.e. in order to get good agreement between calculated energy and observed energy of molecules he multiplied the theoretical value of energy by a scale factor. It is not clear how reasonable this procedure is. Although Davidson et al[30] used Wiberg's parameters in their CNDO calculation they did not use his linear adjustment of energy values; instead they used the calculated energies which are obtained from the usual CNDO procedure. Fischer and Kollmar[31] reparametrized the CNDO method and obtained good heats of atomization, equilibrium geometries and force constants. For penetration they have used the formula

$$V_{AB} = Z_B \quad (1-\alpha)\ \Gamma_{AB} + \alpha\sqrt{R_{AB}^2 + 1/\mu_A^2} \qquad \text{(III-20)}$$

where $\alpha=0.22$ and μ_A is the orbital exponent. Although the equation (III-20) works well when R is small it is doubtful how far this equation will be successful when R is large as in large molecules. Theoretically, the equation (III-20) is not sound because when $R \to \infty$, $V_{AB} \to \infty$ whereas in reality when $R \to \infty$, $V_{AB} \to 0$. In order to obtain good results, they have changed the functional forms for resonance integrals and certain nuclear

attraction integrals from those in CNDO/2. They have adjusted a total of eight parameters and the requirement of hybridization invariance was relaxed.

Dewar and Klopman[19] and Dewar et al[19a] calculated heats of formation of a large number of hydrocarbons by using PNDO (Partial Neglect of Differential Overlap) and MINDO (Modified Intermediate Neglect of Differential Overlap) methods by introducing rather artificial nuclear-nuclear energy repulsion terms. Although the results were in good agreement with experiment, how such an ad hoc approximation is justified in order to get good heats of formation is far from obvious. It is also seen that such an approximation yields unrealistically short values for bond length. Thus the net result is to sacrifice one at the cost of the other.

The choice of parameters or mode of evaluation of certain integrals discussed so far is useful only for the study of ground state properties of molecules and cannot be utilized in predicting the spectral transitions. Thus the conflict between ground state properties and spectroscopic properties also exists in all-valence-electron methods as well as in the MO theory for π systems. Thus it would not be good to transfer certain parameters

for the study of certain properties to the study of others because they account for different physical properties.

Del Bene and Jaffé[32] using limited configuration interaction studied the spectra of benzene, pyridine and some related molecules. They also used different β's for σ and π. Although they are successful in predicting the spectra of some conjugated systems, the method fails to predict correct heats of formation and molecular geometries. They adopted the CNDO method for the calculation of the energy levels of those molecules and their aim was to gain information on the effect of the σ electrons on the π energy levels.

So far in all these methods a minimum basis set of valence shell A.O. has been used. Hence these methods could not account for transitions involving a change in principal quantum number. Salahub and Sandorfy[33] used higher orbitals of H (H_{2s}; H_{2p}) and C (C_{3p}.....) in the CNDO method for some paraffins and obtained reasonable interpretations of the main characteristics of the observed electronic spectra.

Hence we can say that CNDO calculations which give good results in molecular geometry, do not give good results in heats of formation and spectra; again when it gives good results in spectra it does not predict ground state properties correctly.

Chapter IV

KLONDIKE FORMULA

There are several different formulas commonly used for the computation of coulomb integrals in semi-empirical molecular orbital calculations.

As described earlier, people have more or less settled for Ohno's formula[28] or Mataga-Nishimoto's formula[27] in the case of the π-electron approximation (P-P-P theory). In the development of the all-valence-electron approximations the situation has been far from settled; some prefer using Roothaan's explicit theoretical formula[13], while others carry over their habit acquired in the π-electron method to the new stage and use either Ohno's[28] or Mataga-Nishimoto's[27] formula. Now that it has become clear that the choice of the formula for the computation of coulomb integrals constitutes an important part of the semi-empirical adjustment of the individual method, it would be convenient if we could have a suitably parametrized formula which would cover continuously the results of Roothaan's[13], Ohno's[28], and Mataga-Nishimoto's[27] formulas. We have succeeded in devising such a new artificial formula for coulomb integrals in our present work. This we call the Klondike formula, which has the following form,

$$(\mu\mu|\nu\nu) = \frac{1}{R + A} \quad \text{in a.u.} \qquad \text{(IV-1)}$$

where R is $R_{\mu\nu}$, the distance between two centers μ and ν, and

$$A = \frac{1}{a_\mu e^{\kappa_\mu R} + a_\nu e^{\kappa_\nu R}} \qquad \kappa_\mu, \kappa_\nu \geq 0$$

where κ_μ and κ_ν are the klondike parameters for μ and ν centers respectively. In the present work we have restricted our considerations to the case $\kappa_\mu = \kappa_\nu = \kappa$. When $\kappa = 0$, the above coulomb integral formula equation (IV-1) is identical to Mataga-Nishimoto's formula.

The value of a_μ can be determined in the following way:

when R = 0

$$(\mu\mu|\nu\nu) = \frac{1}{A} = a_\mu + a_\nu$$

when the two functions are identical i.e. when $\mu = \nu$

$$(\mu\mu|\mu\mu) = 2a_\mu$$

For Roothaan's method the value of $(\mu\mu|\mu\mu)$ is determined explicitly. For Mataga-Nishimoto's method or Ohno's method $(\mu\mu|\mu\mu)$ is equal to $I_\mu - A_\mu$.

Thus

$$a_\mu = \frac{1}{2}(I_\mu - A_\mu) = (\mu\mu|\mu\mu)$$

We are designating the method using the Klondike formula as CNDOK and the method using Roothaan's formula as CNDOR.

In our parametrization we have found that when $\kappa=0.4$, the Klondike formula corresponds to Ohno's formula and when $\kappa= 0.8$, it corresponds to Roothaan's formula.

Table (1) compares the values of $\Gamma_{1s1s'}$ $\Gamma_{2s2s'}$ and Γ_{2s1s} calculated by the Klondike formula and Ohno's formula. Figures 1, 3, 5 represent the variation of Γ values with R. From these figures it is seen that in all cases the curve of the Klondike formula agrees well with that of Ohno. In the case of Γ_{1s1s} deviation between the Klondike and Ohno curves is appreciable at small internuclear distances. This is not significant because molecules do not exist with such small internuclear distances at equilibrium.

Table (2) contains the values of $\Gamma_{1s1s'}$ $\Gamma_{2s2s'}$ and Γ_{2s1s} calculated by the Klondike formula and Roothaan's formula and figures 2, 4, 6 are also drawn for comparison. It is seen that for Γ_{1s1s} the two methods agree well at all internuclear distances. But for $\Gamma_{2s1s'}$ $\Gamma_{2s2s'}$ large deviations are observed at small values of R. As stated earlier this has little effect in the calculations because no molecule exists with such small internuclear distances.

Table (1)

Results of Γ integrals for different internuclear distances (in a.u) when κ=0.4

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R	i)	ii)	i)	ii)	i)	ii)
0.1	0.47202	0.46878	0.39579	0.39595	0.43392	0.43250
0.2	0.47045	0.46436	0.39487	0.39518	0.43270	0.43003
0.3	0.46787	0.45937	0.39334	0.39384	0.43069	0.42697
0.4	0.46432	0.45386	0.39122	0.39196	0.42792	0.42337
0.5	0.45988	0.44791	0.38856	0.38957	0.42443	0.41928
0.6	0.45463	0.44157	0.38537	0.38671	0.42029	0.41474
0.7	0.44864	0.43490	0.38170	0.38343	0.41554	0.40981
0.8	0.44202	0.42796	0.37760	0.37976	0.41027	0.40455
0.9	0.43485	0.42080	0.37310	0.37575	0.40452	0.39899
1.0	0.42725	0.41347	0.36827	0.37143	0.39837	0.39318
1.1	0.41929	0.40602	0.36313	0.36685	0.39190	0.38717
1.2	0.41106	0.39849	0.35775	0.36203	0.38515	0.38100

Table (1) (Cont'd.)

R	Γ_{1s1s} i)	Γ_{1s1s} ii)	Γ_{2s2s} i)	Γ_{2s2s} ii)	Γ_{2s1s} i)	Γ_{2s1s} ii)
1.3	0.40264	0.39091	0.35216	0.35703	0.37820	0.37470
1.4	0.39411	0.38332	0.34641	0.35186	0.37111	0.36830
1.5	0.38552	0.37574	0.34053	0.34656	0.36391	0.36185
1.6	0.37694	0.36821	0.33457	0.34116	0.35666	0.35536
1.7	0.36840	0.36074	0.32856	0.33568	0.34940	0.34886
1.8	0.35995	0.35335	0.32252	0.33016	0.34217	0.34238
1.9	0.35162	0.34606	0.31649	0.32461	0.33499	0.33594
2.0	0.34344	0.33888	0.31048	0.31904	0.32789	0.32954
2.1	0.33542	0.33183	0.30452	0.31349	0.32090	0.32321
2.2	0.32759	0.32491	0.29863	0.30796	0.31402	0.31696
2.3	0.31996	0.31813	0.29281	0.30247	0.30728	0.31079
2.4	0.31253	0.31150	0.28708	0.29703	0.30068	0.30473
2.5	0.30531	0.30502	0.28146	0.29165	0.29423	0.29877

Table (1) (Cont'd.)

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R	i)	ii)	i)	ii)	i)	ii)
2.6	0.29830	0.29869	0.27594	0.28634	0.28794	0.29293
2.7	0.29150	0.29251	0.27053	0.28111	0.28182	0.28720
2.8	0.28492	0.28649	0.26525	0.27596	0.27586	0.28159
2.9	0.27855	0.28063	0.26008	0.27090	0.27006	0.27611
3.0	0.27238	0.27492	0.25504	0.26593	0.26443	0.27075
3.1	0.26642	0.26937	0.25013	0.26106	0.25897	0.26551
3.2	0.26066	0.26397	0.24534	0.25628	0.25366	0.26041
3.3	0.25509	0.25871	0.24068	0.25161	0.24852	0.25542
3.4	0.24970	0.25360	0.23614	0.24704	0.24353	0.25057
3.5	0.24450	0.24864	0.23172	0.24257	0.23870	0.24583
3.6	0.23947	0.24382	0.22743	0.23820	0.23401	0.24123
3.7	0.23461	0.23914	0.22325	0.23394	0.22947	0.23674
3.8	0.22991	0.23459	0.21919	0.22977	0.22507	0.23237
3.9	0.22537	0.23017	0.21525	0.22571	0.22080	0.22811

Table (1) (Cont'd.)

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R	i)	ii)	i)	ii)	i)	ii)
4.0	0.22098	0.22587	0.21141	0.22174	0.21667	0.22397
4.1	0.21674	0.22170	0.20769	0.21788	0.21266	0.21994
4.2	0.21263	0.21766	0.20407	0.21411	0.20878	0.21602
4.3	0.20866	0.21372	0.20055	0.21043	0.20502	0.21221
4.4	0.20482	0.20990	0.19713	0.20685	0.20137	0.20850
4.5	0.20110	0.20619	0.19381	0.20336	0.19783	0.20489
4.6	0.19749	0.20259	0.19058	0.19996	0.19440	0.20138
4.7	0.19401	0.19909	0.18744	0.19665	0.19107	0.19797
4.8	0.19063	0.19569	0.18439	0.19342	0.18784	0.19465
4.9	0.18736	0.19238	0.18142	0.19027	0.18471	0.19141
5.0	0.18418	0.18916	0.17853	0.18721	0.18166	0.18827

i) using Ohno's formula for Γ integrals

ii) using the Klondike formula for Γ integrals

Table (2)

Results of Γ integrals for different internuclear distances (in a.u) when κ=0.8

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R	i)	ii)	i)	ii)	i)	ii)
0.1	0.74856	0.75142	0.58977	0.60075	0.64725	0.67669
0.2	0.74430	0.74840	0.58811	0.60816	0.64508	0.67942
0.3	0.73736	0.74138	0.58535	0.61227	0.64148	0.67839
0.4	0.72794	0.73089	0.58154	0.61321	0.63648	0.67394
0.5	0.71631	0.71748	0.57671	0.61120	0.63011	0.66646
0.6	0.70276	0.70173	0.57093	0.60651	0.62246	0.65636
0.7	0.68761	0.68418	0.56424	0.59947	0.61359	0.64410
0.8	0.67115	0.66531	0.55671	0.59042	0.60361	0.63012
0.9	0.65369	0.64558	0.54842	0.57971	0.59263	0.61482
1.0	0.63550	0.62535	0.53943	0.56768	0.58077	0.59857
1.1	0.61683	0.60494	0.52982	0.55463	0.56817	0.58171
1.2	0.59790	0.58462	0.51967	0.54084	0.55497	0.56450
1.3	0.57892	0.56457	0.50906	0.52657	0.54130	0.54718
1.4	0.56003	0.54495	0.49807	0.51203	0.52730	0.52995

Table (2) (Cont'd.)

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R	i)	ii)	i)	ii)	i)	ii)
1.5	0.54140	0.52588	0.48678	0.49739	0.51307	0.51294
1.6	0.52311	0.50743	0.47526	0.48280	0.49875	0.49628
1.7	0.50528	0.48966	0.46359	0.46838	0.48444	0.48006
1.8	0.48796	0.47261	0.45185	0.45422	0.47022	0.46433
1.9	0.47120	0.45628	0.44009	0.44039	0.45618	0.44915
2.0	0.45505	0.44068	0.42838	0.42695	0.44238	0.43453
2.1	0.43952	0.42580	0.41677	0.41393	0.42888	0.42049
2.2	0.42463	0.41163	0.40532	0.40135	0.41573	0.40704
2.3	0.41038	0.39813	0.39406	0.38923	0.40297	0.39416
2.4	0.39676	0.38529	0.38303	0.37757	0.39061	0.38185
2.5	0.38376	0.37307	0.37226	0.36638	0.37868	0.37010
2.6	0.37138	0.36146	0.36178	0.35565	0.36719	0.35888
2.7	0.35958	0.35041	0.35161	0.34537	0.35614	0.34817

Table (2) (Cont'd.)

	Γ_{1s1s}		Γ_{2s2s}		Γ_{2s1s}	
R	i)	ii)	i)	ii)	i)	ii)
2.8	0.34835	0.33991	0.34175	0.33552	0.34553	0.33796
2.9	0.33766	0.32992	0.33222	0.32610	0.33536	0.32823
3.0	0.32750	0.32041	0.32303	0.31708	0.32563	0.31894
3.1	0.31783	0.31137	0.31417	0.30846	0.31631	0.31008
3.2	0.30863	0.30275	0.30565	0.30021	0.30740	0.30162
3.3	0.29989	0.29454	0.29746	0.29232	0.29889	0.29356
3.4	0.29156	0.28671	0.28960	0.28477	0.29076	0.28585
3.5	0.28364	0.27925	0.28205	0.27754	0.28299	0.27849
3.6	0.27609	0.27212	0.27482	0.27063	0.27558	0.27146
3.7	0.26890	0.26532	0.26788	0.26400	0.26849	0.26474
3.8	0.26204	0.25881	0.26123	0.25766	0.26172	0.25830
3.9	0.25551	0.25260	0.25486	0.25158	0.25525	0.25215
4.0	0.24927	0.24665	0.24875	0.24576	0.24906	0.24625
4.1	0.24331	0.24095	0.24290	0.24017	0.24315	0.24061

Table (2) (Cont'd.)

	Γ 1s1s		Γ 2s2s		Γ 2s1s	
R	i)	ii)	i)	ii)	i)	ii)
4.2	0.23761	0.23550	0.23729	0.23480	0.23748	0.23519
4.3	0.23217	0.23027	0.23192	0.22966	0.23207	0.23000
4.4	0.22696	0.22525	0.22676	0.22471	0.22688	0.22501
4.5	0.22197	0.22044	0.22181	0.21996	0.22190	0.22023
4.6	0.21718	0.21581	0.21707	0.21539	0.21714	0.21563
4.7	0.21260	0.21137	0.21251	0.21099	0.21256	0.21120
4.8	0.20820	0.20710	0.20813	0.20676	0.20817	0.20695
4.9	0.20397	0.20299	0.20392	0.20269	0.20395	0.20286
5.0	0.19991	0.19903	0.19987	0.19877	0.19989	0.19891

i) using Roothaan's formula for Γ integrals

ii) using the Klondike formula for Γ integrals

Comparison of Γ_{1s1s} values of Klondike with those of Ohno's and Roothaan's

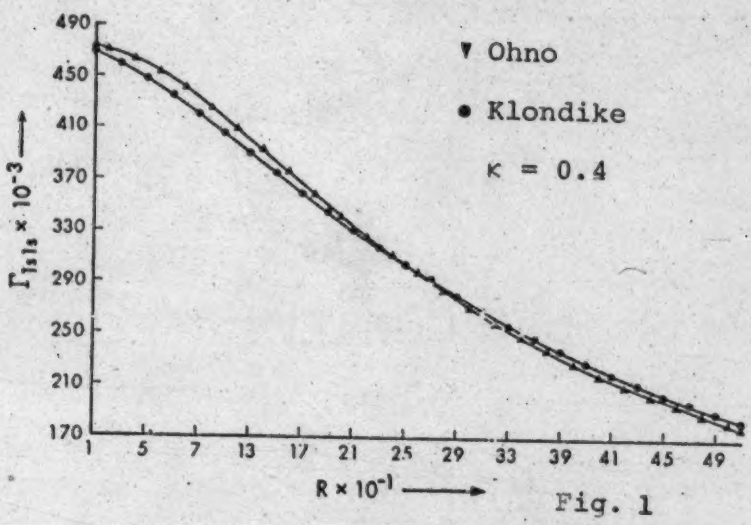


Fig. 1

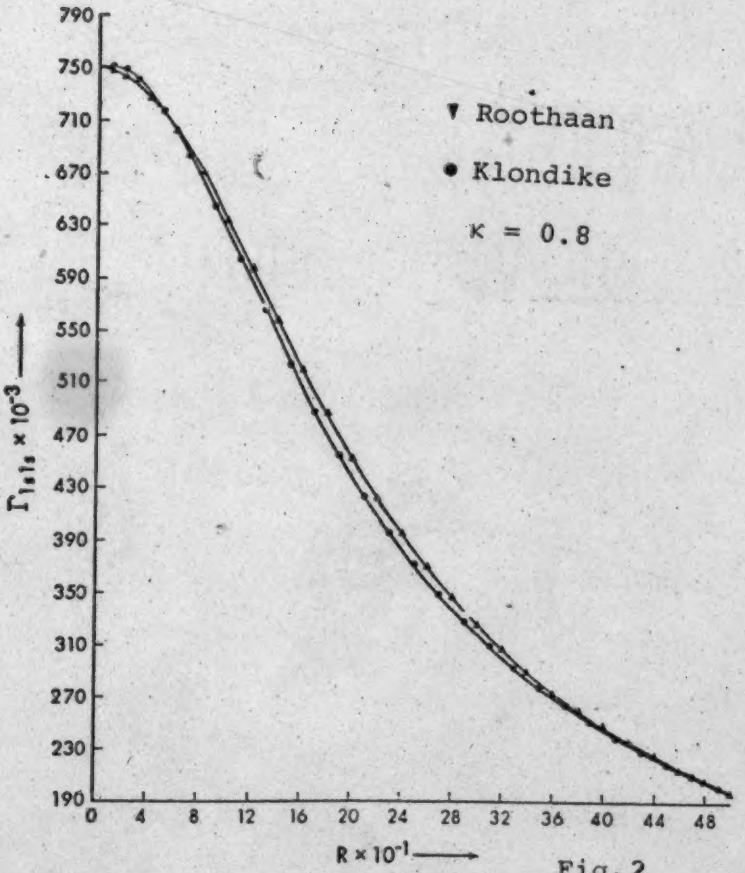


Fig. 2

Comparision of Γ_{2s2s} values of Klondike with those of Ohno's and Roothaan's

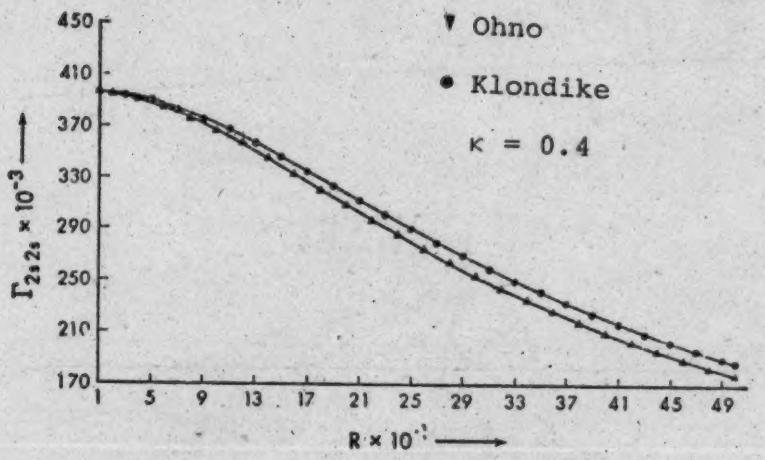


Fig. 3

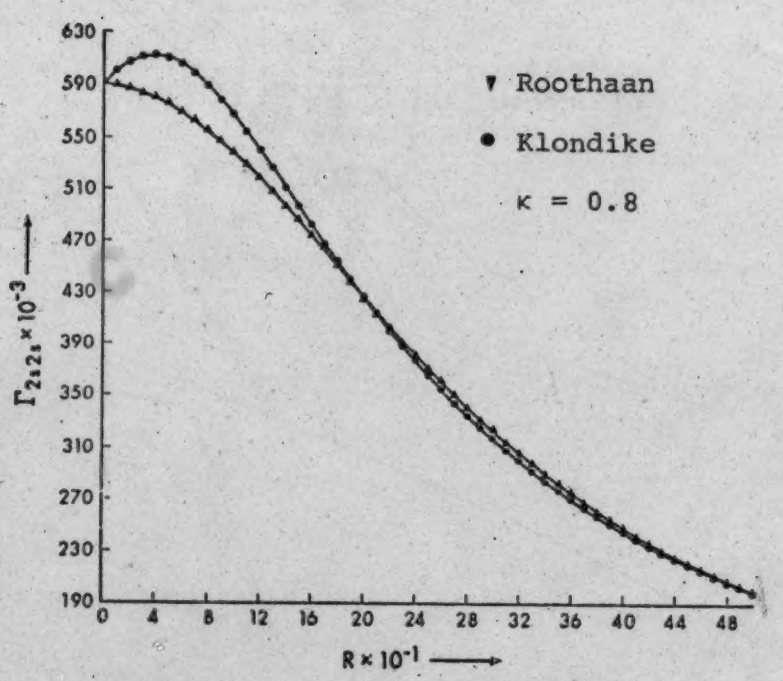


Fig. 4

Comparison of Γ_{2s1s} values of Klondike with those of Ohno's and Roothaan's

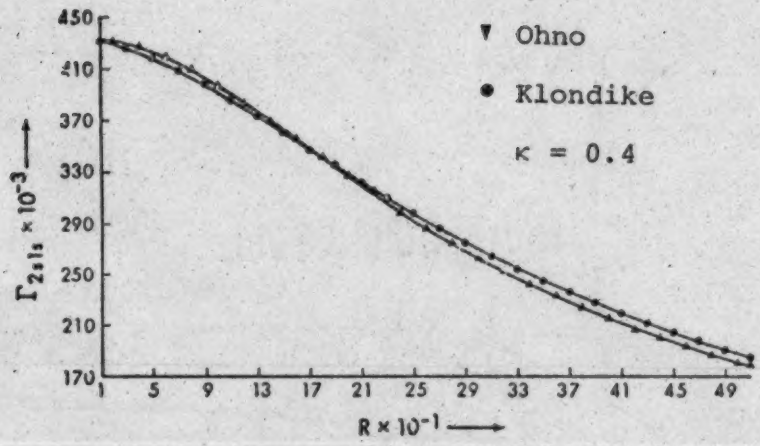


Fig. 5

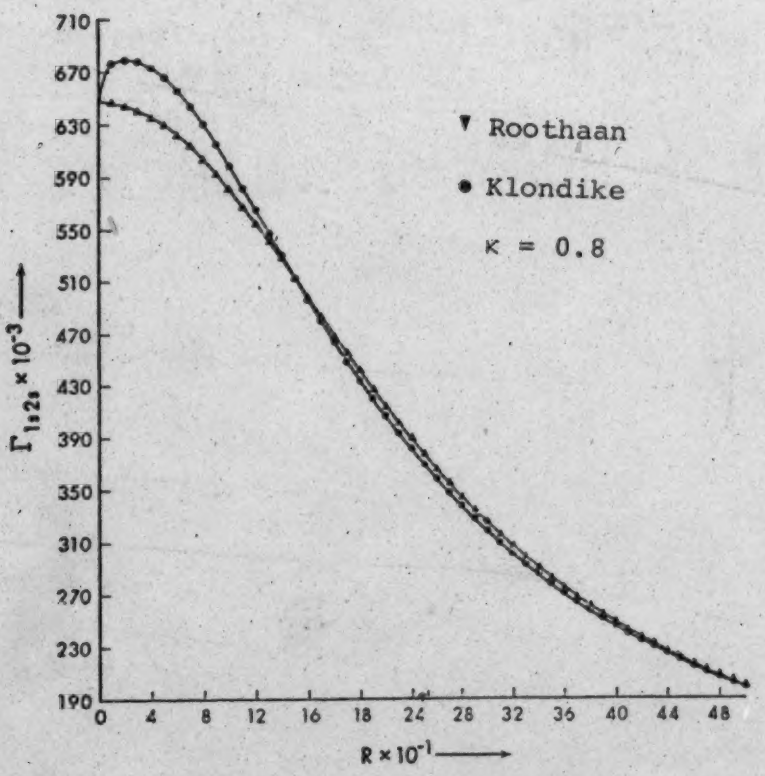


Fig. 6

In the main body of the present work, Roothaan's formulas are used in accordance with the widely accepted CNDO/2 method. However, we shall also describe our preliminary attempt to use the Klondike formula in conjunction with the CNDO approximation.

Chapter V

A NEW PARAMETRIZATION OF ALL-VALENCE-ELECTRON THEORY

In all-valence-electron methods at the level of CNDO approximation, the parametrization and choice of parameters are of central importance. A particular choice of parameters can predict certain properties of a molecule which are in good agreement with experimental results. However, use of the same parameters may cause other predicted properties to disagree with experimental values. One of the most serious examples is the dilemma between good bond lengths and good heats of formation as mentioned in Chapter III. In this work we have made an attempt to parametrize the theory in a way to obtain good correlation between energies and bond lengths of some hydrocarbons such as methane, ethane, propane, butane, ethylene, allene, acetylene and benzene.

Description of the Method:

The present method is similar to the CNDO/2 method which has been described earlier. Here we are going to discuss the essential features of the present method.

In the SCF-LCAO-MO theory the molecular orbitals are determined by solving the Hartree-Fock-Roothaan SCF

equation

$$\mathbf{F\,C} = \mathbf{S\,C\,E} \qquad \text{(V-1)}$$

where $\mathbf{C}$ is the matrix of the coefficients $C_{i\mu}$, $\mathbf{E}$ is the eigenvalue matrix of orbital energies and $\mathbf{S}$ is the overlap integral matrix.

The elements of the Fock matrix $F_{\mu\nu}$ may be split up into two parts

$$F_{\mu\nu} = H_{\mu\nu} + G_{\mu\nu} \qquad \text{(V-2)}$$

where

$$H_{\mu\nu} = \int \mu(1) \left[-\tfrac{1}{2}\nabla^2 - \sum_A V_A \right] \nu(1)\, dv \qquad \text{(V-3)}$$

(one-electron part)

and

$$G_{\mu\nu} = \sum_{\lambda,\sigma} P_{\lambda\sigma} \left[(\mu\nu|\lambda\sigma) - \tfrac{1}{2}(\mu\sigma|\nu\lambda) \right] \qquad \text{(V-4)}$$

(two-electron part)

Here

$$P_{\lambda\sigma} = 2 \sum_{i}^{occ} C_{\lambda i}\, C_{\sigma i} \qquad \text{and}$$

$$(\mu\nu|\lambda\sigma) = \iint \mu(1)\ \lambda(2) \left(\frac{1}{r_{12}} \right) \nu(1)\sigma(2)\, dv_1 dv_2 \qquad \text{(V-5)}$$

The diagonal elements $H_{\mu\mu}$ may be divided into two parts. One is an atomic term and the other is the interaction of the electrons in χ_μ with the cores of all other atoms.

$$H_{\mu\mu} = (\mu|-\tfrac{1}{2}\nabla^2-V_A|\mu)-\sum_{B\neq A}(\mu|V_B|\mu) \qquad \text{(V-6)}$$

The off-diagonal elements $H_{\mu\nu}$ are given by

$$H_{\mu\nu} = \frac{1}{2}(\beta^\circ_\mu+\beta^\circ_\nu) \; S_{\mu\nu} \qquad \text{(V-7)}$$

We have approximated the second term in $H_{\mu\mu}$ by the relation

$$(\mu|V_B|\mu) = Z_B\,(1-\lambda e^{-\omega R_{AB}})\,\Gamma_{AB} \qquad \text{(V-8)}$$

where Z_B is the core charge on atom B equal to the nuclear charge minus the number of inner shell electrons, Γ_{AB} is the electron repulsion integral and λ and ω are global parameters which we introduce in the present work. The justification of the formula in (V-8) will be discussed shortly. Since

$$S_{\mu\nu} = \delta_{\mu\nu} \text{ (except in } H_{\mu\nu})$$

$G_{\mu\mu}$ takes the form

$$G_{\mu\mu} = \sum_{\lambda} P_{\lambda\lambda} (\mu\mu|\lambda\lambda) - \frac{1}{2} P_{\mu\mu} (\mu\mu|\mu\mu) \qquad \text{(V-9)}$$

where the summation is over all basis functions and

$$G_{\mu\nu} = \frac{1}{2} P_{\mu\nu} (\mu\mu|\nu\nu) \qquad \text{(V-10)}$$

Here $P_{\mu\mu}$ refers to the diagonal elements of the bond order matrix i.e. the electron density in a given orbital.

In order to justify the modifications in the CNDO method introduced in this work and to evaluate certain parameters and integrals we would like to make the following comments:

(1) In principle, the one-electron part can be computed within a reasonable time, with the possible exception of three-center integral

$$H_{\mu\mu} = (\mu|-\frac{1}{2}\nabla^2 - \sum_{A} V_A|\mu)$$

$$= (\mu|-\frac{1}{2}\nabla^2 - V_A|\mu) - \sum_{B \neq A} (\mu|V_B|\mu) \qquad \text{(V-11)}$$

$$H_{\mu\nu} = (\mu|-\frac{1}{2}\nabla^2 - \sum_{A} V_A|\nu) \qquad \text{(V-12)}$$

If μ and ν are on the same atom and μ or ν represents one of s, p_x, p_y, p_z, then $H_{\mu\nu} = 0$ (this is not an approximation). Thus

$$H_{\mu\nu} = (\mu|-\tfrac{1}{2}\nabla^2-V_A-V_B|\nu) - \sum_{C\neq A,B} (\mu|V_C|\nu) \qquad \text{(V-13)}$$

(μ on A, ν on B)

If appropriate expressions are given to $\{V_A\}$, $H_{\mu\mu}$ and $H_{\mu\nu}$ may be computed explicitly, but we introduce a series of approximations. A primary reason for this is that we attempt necessary adjustments to the drastic approximations in the two-electron parts. Essentially, the one-electron part of the total energy is negative and the two-electron part is necessarily positive because they correspond to the repulsive electron-electron interaction energy. Thus any change in this positive contribution must definitely be counterbalanced by the negative contribution from the one-electron part. In order to incorporate this feature into the formulas we have introduced the approximation

$$(\mu|V_B|\mu) = Z_B\,(1-\lambda e^{-\omega R_{AB}})\,\Gamma_{AB}$$

where in the present investigation λ and ω are treated as global parameters. While this explicit formula is something to be debated, the logic behind it as described above is straightforward and seems to be difficult to reject. Another obvious compensation we may make, would be to drop

$$-\sum_{C\neq A,B}(\mu|V_C|\nu)$$

in $H_{\mu\nu}$ because the corresponding three-center two-electron integral, say $(\mu_A\nu_B|\sigma_C\sigma_C)$ is also dropped by the ZDO approximation.

(2) In the P-P-P method, various approximations have been used for $(\mu\mu|\mu\mu)$ and $(\mu\mu|\lambda\lambda)$. It may be said that reduced values for $(\mu\mu|\mu\mu)$ arise from the empirical evaluation and for $(\mu\mu|\lambda\lambda)$ convenient approximate formulas are used, the most popular ones being Mataga-Nishimoto's[27] and Ohno's[28].

In the all-valence-electron method, the situation is somewhat different. Pople and his school make use of explicit Roothaan formulas for coulomb integrals. Clark and Ragle[34] contend that one should not use Mataga-Nishimoto type approximations because they would introduce some inconsistency in the CNDO method. However,

other workers such as Del Bene and Jaffé[32], Dewar and Klopman[19] use those approximate formulas for coulomb integrals rather freely.

In the present work we have attempted to unify these two distinct approaches by introducing a new approximate coulomb integral formula which we call the Klondike formula, as we discussed earlier.

(3) $U_{\mu\mu}$ are the atomic matrix elements of the one-electron Hamiltonian. It includes the core potential of the atom to which χ_μ belongs. It can be calculated from approximate atomic orbitals or it can be estimated semi-empirically from experimental data on atomic energy levels. It can also be used as an empirical parameter. Pople[17] approximated it from atomic spectroscopy. According to the differential overlap approximation all electronic states of a given configuration have the same energy. Thus

$$E\ (X,\ 2s^m 2p^n) = m U_{2s} + n U_{2p} + \frac{1}{2}(m+n)(m+n-1)\Gamma_{xx} + C \qquad (V\text{-}14)$$

where term C comes from the inner electrons. In order to calculate $U_{\mu\mu}$ from the experimental data, it is

therefore required to consider an average energy of all the states of the configuration. In order to calculate the single U_μ the proper ionization process should be considered.

$$I_s(X, 2s^m 2p^n) = E(X^+, 2s^{m-1}2p^n) - E(X, 2s^m 2p^n)$$
$$= -U_{2s} - (m+n-1)\,\Gamma_{xx} \qquad \text{(V-15)}$$

An atomic orbital has the tendency to acquire and lose electrons and this tendency of the atomic orbital can be accounted for by the molecular orbital theory. As a result in CNDO/2 the following equations

$$-I_\mu = U_{\mu\mu} + (Z_x - 1)\,\Gamma_{xx} \qquad \text{(V-16)}$$

$$-A_\mu = U_{\mu\mu} + Z_x\,\Gamma_{xx} \qquad \text{(V-17)}$$

have been averaged to calculate $U_{\mu\mu}$. Thus

$$U_{\mu\mu} = -\frac{1}{2}(I_\mu + A_\mu) - (Z_\mu - \tfrac{1}{2})\Gamma_{xx} \qquad \text{(V-18)}$$

It is quite clear that the core parameters of CNDO/2 are uniformly too negative whereas the parameters of CNDO/1 are less negative than CNDO/2. We have used $U_{\mu\mu}$ as an empirical parameter in our calculations.

(4) If we can write molecular orbital ψ_i as a linear combination of atomic orbitals i.e.

$$\psi_i = \sum_{\mu} C_{\mu i} \chi_{\mu} \qquad \text{(V-19)}$$

and if ψ_i can be written as a linear combination of another basis set χ'_{α} then there are also linear combination of the orbital χ_{μ}

$$\chi'_{\alpha} = \sum_{\mu\alpha} t_{\mu\alpha} \chi_{\mu} \qquad \text{(V-20)}$$

where $t_{\mu\alpha}$ is a non-singular matrix.

There are three types of transformation:

(a) Transformations which only mix atomic orbitals on the same atom with same n and l. An important transformation is the coordinate transformation.

(b) Transformations which only mix atomic orbitals on the same atom with different l. The resulting orbitals are known as atomic hybrid orbitals.

(c) Transformations which mix atomic orbitals on different atoms leading to a non-atomic basis set.

For molecules of low symmetry coordinate invariance is an essential feature. However, invariance to hybridization is less important.

Using the ZDO approximation in one frame, in another frame using the condition of equation (V-20) invariance can be proved as follows:

$$(\alpha\beta|\gamma\delta)=\sum_{\mu}\sum_{\nu}\sum_{\lambda}\sum_{\sigma} t_{\mu\alpha}t_{\nu\beta}t_{\lambda\gamma}t_{\sigma\delta}\ (\mu\nu|\lambda\sigma) \qquad \text{(V-21)}$$

If the zero differential condition is applicable to the old basis set, the integral $(\mu\nu|\lambda\sigma)$ will be $\delta_{\mu\nu}\delta_{\lambda\sigma}$. Therefore,

$$(\alpha\beta|\gamma\delta) = \sum_{\mu}\sum_{\lambda} t_{\mu\alpha}t_{\mu\beta}t_{\lambda\gamma}t_{\lambda\delta}\ (\mu\mu|\lambda\lambda) \qquad \text{(V-22)}$$

If we allow pure coordinate rotation only, then S does not change and only P_x, P_y, P_z rotate inside the sub-group. Therefore,

$$\left[\begin{array}{c|c} 1 & 0 \\ \hline 0 & t \end{array}\right] \begin{bmatrix} S \\ P_x \\ P_y \\ P_z \end{bmatrix} = \begin{bmatrix} S \\ P'_x \\ P'_y \\ P'_z \end{bmatrix}$$

If we assume $\mu=S_A$, $\lambda=S_B$ then

$$t_{\mu\alpha}{}^{\rightarrow\delta}{}_{\mu\alpha},\ t_{\mu\beta}{}^{\rightarrow\delta}{}_{\mu\beta},\ t_{\lambda\gamma}{}^{\rightarrow\delta}{}_{\lambda\gamma},\ t_{\lambda\delta}{}^{\rightarrow\delta}{}_{\lambda\delta} \text{ and finally}$$

$$(\alpha\beta|\gamma\delta) \quad \rightarrow \quad (S_A S_A|S_B S_B)$$

Of course, this was evident from the beginning. For the next step

$$\mu = S_A,\ \lambda = P_B \text{ on B} \quad (3 \text{ components})$$

then

$$(S_A S_A|\gamma\delta) = \sum_{\lambda} t_{\lambda\gamma}\ t_{\lambda\delta}\ (S_A S_A|\lambda\lambda)$$

If we put

$$\Gamma_{S(A)P(B)} = (S_A S_A|P_{xB}P_{xB}) = (S_A S_A|P_{yB}P_{yB})$$

$$= (S_A S_A|P_{zB}P_{zB})$$

Then in the above equation

$$(S_A S_A|\gamma\delta) = \Gamma_{S(A)P(B)} \sum_{\lambda} t_{\lambda\gamma}\ t_{\lambda\delta}$$

$$\doteq \Gamma_{S(A)P(B)}\,\delta_{\gamma\delta} \qquad \text{(V-23)}$$

so that invariance is proved.

If $\mu=P_A$, $\lambda=P_B$ and if we put

$$\Gamma_{P(A)P(B)} = (P_{x(A)}P_{X(A)}|P_{x(B)}P_{x(B)})$$
$$= (P_{x(A)}P_{x(A)}|P_{y(B)}P_{y(B)})$$
$$= (P_{x(A)}P_{x(A)}|P_{z(B)}P_{z(B)})$$
$$= \ldots\ldots\ldots \quad 3 \times 3 \text{ manifold}$$

then $$(\alpha\beta|\gamma\delta) = \sum_{\mu}\sum_{\lambda} t_{\mu\alpha}\, t_{\mu\beta}\, t_{\lambda\gamma}\, t_{\lambda\delta}\, \Gamma_{P(A)P(B)}$$

$$= \Gamma_{P(A)P(B)}\, \delta_{\alpha\beta}\, \delta_{\gamma\delta} \qquad (V\text{-}24)$$

Invariance is proved again.

In the two center terms $(\mu|V_B|\mu)$ and $(\mu|V_B|\nu)$, monatomic differential overlap $\chi_\mu\,\chi_\nu$ $(\mu\neq\nu)$ on atom A suggests that $(\mu|V_B|\nu)$ is equal to zero. According to the invariance condition for all χ_μ in A, the diagonal elements $(\mu|V_B|\mu)$ are the same. For the same reason as in Γ_{AB} we can write

$$(\mu|V_B|\mu) = V_{AB} \qquad (V\text{-}25)$$

In the CNDO method the resonance integrals, $\beta_{\mu\nu}$, are evaluated semi-empirically. Here also the invariance condition has been satisfied by assuming that $\beta_{\mu\nu}$ is proportional to the overlap integral.

$$H_{\mu\nu} = \frac{1}{2} (\beta_{\mu}^{\circ} + \beta_{\nu}^{\circ}) S_{\mu\nu} \qquad \text{(V-26)}$$

As overlap increases, the bonding capacity of the overlap also increases. To satisfy the invariance condition it is required that for all atomic orbitals the proportionality factor between $H_{\mu\nu}$ and $S_{\mu\nu}$ is the same. The constants are denoted by β_{μ}°, β_{ν}° and depend on the nature of atom μ and ν; $\beta^{s}, \beta^{p}, \beta^{d}$ may be prepared for each atom. In the present work we parametrize the theory in such a way that it encompasses these possibilities.

Computational Method and Parametrization:

We have developed an all-valence-electron computer program at the CNDO level of approximation. Our program can handle the following atomic orbitals and atomic parameters:

Atomic Orbitals:

H	1s, $2p_x$, $2p_y$, $2p_z$
Li, Be, B, C, N, O, F	2s, $2p_x$, $2p_y$, $2p_z$
Na, Mg, Al, Si, P, S, Cl	3s, $3p_x$, $3p_y$, $3p_z$

Atomic Parameters:

Z (effective charge)

U_s, U_{p_x}, U_{p_y}, U_{p_z}

β_s, β_{p_x}, β_{p_y}, β_{p_z}

a_s, a_{p_x}, a_{p_y}, a_{p_z} { For Roothaan's formula $a=\frac{1}{2}(I+A)$ / For Klondike formula $a=(I-A)$ }

ζ_s, ζ_{p_x}, ζ_{p_y}, ζ_{p_z} (Orbital Exponent)

κ (for Klondike formula)

λ , ω

The above 20 parameters can be assigned to each atom but κ, λ, ω are used as global parameters in the present work.

Mostly we have used 1s orbitals for H and 2s, $2p_x$, $2p_y$ and $2p_z$ orbitals for carbon. We have also tested the effect of inclusion of higher orbitals such as $2p_x$, $2p_y$, and $2p_z$ orbitals on hydrogen in the case of benzene and we have compared the coefficients with those reported by Kern[35].

Although agreement between these two sets is not so good, still we hope that inclusion of higher orbitals will give good results in the prediction of electronic transitions leading to an excited state with considerable Rydberg character as Salahub and Sandorfy[33] did in the case of saturated paraffin.

It should be obvious that the parametrization of the present computational program is a very flexible one. For a general molecular geometry the constraints placed upon the parameters due to invariance requirements may be classified as follows:

(1) Both space (coordinate) invariance and hybridization invariance

$$U_s, \quad U_{p_x} = U_{p_y} = U_{p_z}$$

$$\beta_s = \beta_{p_x} = \beta_{p_y} = \beta_{p_z}$$

$$a_s = a_{p_x} = a_{p_y} = a_{p_z}$$

$$\zeta_s = \zeta_{p_x} = \zeta_{p_y} = \zeta_{p_z}$$

(2) Space invariance only

$$U_s, \quad U_{p_x} = U_{p_y} = U_{p_z}$$

$$\beta_s, \quad \beta_{p_x} = \beta_{p_y} = \beta_{p_z}$$

$$a_s, \quad a_{p_x} = a_{p_y} = a_{p_z}$$

$$\zeta_s, \quad \zeta_{p_x} = \zeta_{p_y} = \zeta_{p_z}$$

(3) Relaxation of hybridization invariance for hydrogen only

For hydrogen case (2)

For all others case (1)

There are, however, a vast number of chemically important molecules which are of planar form with the σ-π distinction. These have been the subject of applications of the immensely popular Pariser-Parr-Pople method. There is no reason for us suddenly to abandon advantages due to the planarity in the all-valence-electron approximation. When the σ-π distinction is possible, the constraints upon the parameters are

(4) Both space and hybridization invariance for σ part

$$U_s, \; U_{p_x} = U_{p_y}, \; U_{p_z}$$

$$\beta_s = \beta_{p_x} = \beta_{p_y}, \; \beta_{p_z}$$

$$a_s = a_{p_x} = a_{p_y}, \; a_{p_z}$$

$$\zeta_s = \zeta_{p_x} = \zeta_{p_y}, \; \zeta_{p_z}$$

(5) Space invariance only

$$U_s, \; U_{p_x} = U_{p_y}, \; U_{p_z}$$

$$\beta_s, \; \beta_{p_x} = \beta_{p_y}, \; \beta_{p_z}$$

$$a_s, \; a_{p_x} = a_{p_y}, \; a_{p_z}$$

$$\zeta_s, \; \zeta_{p_x} = \zeta_{p_y}, \; \zeta_{p_z}$$

(6) Relaxation of hybridization invariance for σ orbitals of hydrogen only

For hydrogen case (5)

For all others case (4)

In the present work these possible flexibilities have been explored only to a limited extent.

Table (3) contains the values of CNDOR parameters along with CNDO/2 parameters for comparison. Aside from the additional global parameters, λ and ω, and the use of different β's for 2s and 2p, there are no drastic changes in our parametrization from that of CNDO/2.

Table (4) contains the values of CNDOK parameters. A preliminary attempt has been made to parametrize CNDOK using κ=0.4 which gives the Ohno's coulomb formula.

The results of both methods have been presented in the next Chapter.

Table (3)

(Parameters in CNDO/2 and CNDOR)

	CNDO/2	CNDOR
Bonding Parameter in ev (β)		
$\beta_H(1s)$	9.0	9.0
$\beta_C(2s)$	21.0	21.0
$\beta_C(2p_x)=\beta_C(2p_y)=\beta_C(2p_z)$	21.0	17.50
Core Parameter in ev (U)		
$U_H(1s)$	17.38	17.06
$U_C(2s)$	70.2713	70.8399
$U_C(2p_x)=U_C(2p_y)=U_C(2p_z)$	61.7923	62.5203
Average Ionization Potential and Electron Affinity in ev (a)		
$a_H(1s)$	7.176	7.176
$a_C(2s)$	14.051	14.051
$a_C(2p)$	5.572	5.572
Orbital Exponent (ζ)		
$\zeta_H(1s)$	1.2	1.16
$\zeta_C(2s)=\zeta_C(2p)$	1.625	1.8
Core Charge (Z)		
$Z_H(1s)$	1	1
$Z_C(2s)=Z_C(2p)$	4	4

Global Parameter

$\lambda_C=\lambda_H=0.136$

$\omega_C=\omega_H=0.75$ a.u.$^{-1}$

Table (4)

(Parameters in CNDOK)

(a) Bonding parameter (β) in ev

β_H	9.0
$\beta_C(2s)=\beta_C(2p_x)=\beta_C(2p_y)=\beta_C(2p_z)$	17.0

(b) Core parameter (U) in ev

$U_H(1s)$	13.06
$U_C(2s)$	51.774
$U_C(2p_x)=U_C(2p_y)=U_C(2p_z)$	43.295

(c) One Center two electron integrals in ev

(I-A) for H (1s)	12.858
(I-A) for C (2s)	10.778
(I-A) for C (2p)	10.778

(d) Orbital exponent (ζ)

$\zeta_H(1s)$	1.2
$\zeta_C(2s) = \zeta_C(2p)$	1.8

(e) Global parameter

$\lambda_C = \lambda_H = -0.343$

$\omega_C = \omega_H = 0.45 \text{ a.u.}^{-1}$

$\kappa_C = \kappa_H = 0.4$

SCF iteration has been carried out in these computations until the difference in electronic energy between two successive iterations is less than 10^{-4} a.u. Convergence to this degree may be achieved within a few cycles. For improper bond lengths of molecules i.e. too large or too small, some difficulty in convergence has been observed. Matrix diagonalization has been performed using the standard Jacobi method.

Overlap integrals have been calculated according to the formulas of Mulliken et al[36] using the exponent values for carbon and Hydrogen noted in Tables (3) and (4).

Two electron integrals have been calculated according to Roothaan's formula[13] in CNDOR and according to the Klondike formula in CNDOK.

Bond angles needed for the calculation of geometry have been taken from Wiberg's[29] paper.

Chapter VI

RESULTS AND DISCUSSION

A. CNDOR Method:

Table (5) contains the calculated total energies for all the molecules studied along with the corresponding CNDO/2 results. It also contains calculated and observed heats of atomization. Table (6) contains the orbital energies calculated by CNDOR along with CNDO/2. Table (7) contains the variation of energy with different bond lengths. Figures (7-14) represent the variation of energy with bond lengths. The bond lengths with minimum energy from the figures are included in Table (8) and the corresponding energy is included in Table (5). Table (8) also contains the bond lengths of the molecules along with the experimental values for comparison.

Heats of Atomization:

From Table (5) it is clear that the energy calculated by the CNDO/2 method is much deeper than that found in the present work.

For comparison with experimental values we have calculated heats of atomization in the following way:

$$E(X,2s^m2p^n) = m\,U_{2s2s} + n\,U_{2p2p} + \frac{1}{2}(m+n)\,(m+n-1)\,\Gamma_{sp}$$

$$\Gamma_{sp} = \frac{1}{2}(\Gamma_{ss} + \Gamma_{pp})$$

$$\Gamma_{2s2s} = \frac{93}{512}\,(\zeta_{2s}+\zeta_{2s}); \qquad \Gamma_{2p2p} = \frac{93}{512}\,(\zeta_{2p}+\zeta_{2p})$$

$$E(H) = U_{1s1s}$$

In our calculation

$$E(H) = -17.06 \text{ ev} = -0.62698 \text{ a.u.}$$

$$E(C) = 2\,U_{2s2s} + 2\,U_{2p2p} + 6\,\Gamma_{sp}$$

$$= -2x\,\frac{70.8399}{27.21} - 2x\,\frac{62.5203}{27.21} + 6x\,\frac{93}{512}\,(1.8+1.8)$$

$$= -5.8789 \text{ a.u.}$$

In the CNDO/2 method

$$E(H) = -17.38 \text{ ev} = -0.63874 \text{ a.u.}$$

$$E(C) = 2\,U_{2s2s} + 2\,U_{2p2p} + 6\,\Gamma_{sp}$$

$$= -2x\,\frac{70.2713}{27.21} - 2x\,\frac{61.7923}{27.21} + 6x\,\frac{93}{512}\,(1.625+1.625)$$

$$= -6.1650 \text{ a.u.}$$

ΔE_{atom} = Number of 'C' atom x E(C) + Number of 'H' atom x E(H)

$\Delta H_{atom} = \Delta E_{atom}$ - Total energy

The heats of atomization calculated by the CNDOR method are in good agreement with the experimental values. On the other hand the agreement between observed heats of atomization and those calculated by CNDO/2 is exceedingly poor. The deviation of our results from the experimental is within 6% in all cases whereas the CNDO/2 deviation varies from 108% to 187%.

Table (5) *

Calculated and Observed Energy

Molecule	TOTAL ENERGY (A) i)	TOTAL ENERGY (A) ii)	TOTAL ENERGY (B) i)	TOTAL ENERGY (B) ii)	ΔE_{atom} i)	ΔE_{atom} ii)
CH_4	- 9.0830	-10.1153	- 9.090	-10.12	- 8.3869	- 8.7199
C_2H_6	-16.7055	-18.8195	-16.710	-18.820	-15.5198	-16.1624
C_2H_4	-15.1952	-17.0675	-15.208	-17.0676	-14.2658	-14.8850
C_2H_2	-13.6899	-15.3411	-13.695	-15.349	-13.0118	-13.6075
C_3H_4	-21.3345	-24.0420	-21.340	-24.0420	-20.1447	-21.0500
C_3H_8	-24.3086	-27.5000	-24.309	-27.505	-22.6527	-23.6049
C_4H_{10}	-31.9129	-36.1940	-31.913	-36.194	-29.7856	-31.0474
C_6H_6	-41.2036	-47.1015	-41.208	-47.1015	-39.0354	-40.8224

Table (5)* (Cont'd.)

Molecule	ΔH_{atom} (A) i)	(A) ii)	(B) i)	(B) ii)	CLASSICAL ΔH_{atom} (C)	in kCal/mol
CH_4	0.6961	1.3954	0.7031	1.4001	0.6693	419.97
C_2H_6	1.1857	2.6571	1.1902	2.6576	1.1350	712.20
C_2H_4	0.9294	2.1825	0.9422	2.1826	0.8979	563.44
C_2H_2	0.6781	1.7336	0.6832	1.7415	0.6478	406.50
C_3H_4	1.1898	2.992	1.1953	2.992	1.1254	706.18
C_3H_8	1.6559	3.8951	1.6563	3.9001	1.6033	1006.07
C_4H_{10}	2.1273	5.1466	2.1274	5.1466	2.0736	1301.20
C_6H_6	2.1682	6.2791	2.1726	6.2791	2.1847	1370.90

i) CNDOR

ii) CNDO/2

* in a.u. if not specified

(A) Calculated

(B) From Figure

(C) From Ref. (29)

Orbital Energies:

Table (6) contains the occupied orbital energies of the molecules studied. We have compared our results with those of Kern[35] for benzene. It is found that the orbital energies calculated by this method are in good agreement with those of Kern[35] who performed an ab initio Hartree-Fock calculation of good accuracy. For comparison we have also included in the table the orbital energies calculated by the CNDO/2 method. Again our results are more reasonable. In particular, the ordering of the orbital energies obtained in the CNDO/2 method does not agree with that of Kern whereas our results are in good agreement. Similar results are also found in the case of ethylene i.e. the orbital energies and the ordering calculated by the CNDOR are superior to those from CNDO/2 when compared to the results of Moskowitz and Harrison[37] who performed SCF calculations with Gaussian basis sets of different sizes. They have shown that the ordering does not change with different basis sets. The orbital energies of their largest basis set for C_2H_4 are included in Table (6).

Table (6) in a.u.

A. Occupied Orbital Energies for C_6H_6: (D_{6h} symmetry)

	CNDOR	Kern's method[35]	CNDO/2
A_{1g}	-1.3996	-1.1487	-1.8728
E_{1u}	-1.1103 -1.1093	-1.0138	-1.3876 -1.3867
E_{2g}	-0.8486 -0.8476	-0.8230	-1.1095 -1.1100
A_{1g}	-0.7571	-0.7081	-1.0632
B_{1u}	-0.5975	-0.6427	-0.8590
B_{2u}	-0.5439	-0.6187	-0.7896
E_{1u}	-0.5214 -0.5194	-0.5872	-0.6968 -0.6964
πA_{2u}	-0.5056	-0.4979	-0.7193
E_{2g}	-0.3951 -0.3946	-0.4946	-0.5158 -0.5154
πE_{1g}	-0.2893 -0.2886	-0.3337	-0.5108 -0.5100

B. Occupied Orbital Energies for C_2H_4 (D_{2h} symmetry)

	CNDOR	Moskowitz & Harrison[37]	CNDO/2
A_g	-1.2094	-1.0581	-1.4061
B_{3u}	-0.8540	-0.8063	-1.0054
B_{2u}	-0.6747	-0.6601	-0.8973
A_g	-0.5624	-0.5829	-0.7147
B_{1g}	-0.4784	-0.5175	-0.5748
πB_{1u}	-0.3873	-0.3815	-0.5836

C. Occupied Orbital Energies for C_3H_4 (D_{2d} symmetry)

	CNDOR	CNDO/2
A_g	-1.1871	-1.4841
B_2	-1.0073	-1.2647
A_g	-0.6813	-0.8767
E	-0.6001 -0.6001	-0.8650 -0.8650
B_2	-0.5392	-0.6929
E	-0.3536 -0.3536	-0.5109 -0.5109

D. Occupied Orbital Energies for C_2H_2 ($C_{\infty v}$ symmetry)

	CNDOR	CNDO/2
A_1	-1.0648	-1.3538
A_2	-0.7163	-0.9755
A_1	-0.5593	-0.7578
E	-0.3781 -0.3781	-0.6418 -0.6418

E. Occupied Orbital Energies for CH_4 (T_d symmetry)

	CNDOR	CNDO/2
A_1	-1.1357	-1.2402
T_2	-0.5976 -0.5974 -0.5974	-0.7171 -0.7169 -0.7169

F. Occupied Orbital Energies for C_2H_6 (D_{3d} symmetry)

	CNDOR	CNDO/2
A_{1g}	-1.2621	-1.5244
A_{2u}	-0.9104	-1.0579
E_u	-0.6658 -0.6658	-0.8870 -0.8870
A_{1g}	-0.5620	-0.6868
E_g	-0.5044 -0.5044	-0.5652 -0.5652

G. Occupied Orbital Energies for C_3H_8 (C_{2v})

	CNDOR	CNDO/2
A_1	-1.3442	-1.6163
B_2	-1.0666	-1.2574
A_1	-0.8824	-1.0624
A_2	-0.7038	-0.9372
A_1	-0.6707	-0.8688
B_2	-0.5857	-0.7519
B_1	-0.5739	-0.7052
A_1	-0.5052	-0.5903
B_2	-0.4917	-0.5808
A_2	-0.4792	-0.5501

H. Occupied Orbital Energies for C_4H_{10} (C_{2h})

	CNDOR	CNDO/2
A_g	-1.3871	-1.6840
B_u	-1.1752	-1.4075
A_g	-0.9456	-1.1138
B_u	-0.8800	-1.0865
A_u	-0.7290	-0.9878
A_g	-0.6444	-0.8425
B_u	-0.6326	-0.8118
B_g	-0.6203	-0.7882
B_u	-0.5395	-0.6516
A_u	-0.5228	-0.6214
A_g	-0.4925	-0.5791
B_g	-0.4736	-0.5511
A_g	-0.4724	-0.5383

Bond Lengths:

On the other hand, the bond lengths Table (8) obtained in this work are in poorer agreement with experiment than those of the CNDO/2 method. Our values are still, in general, more reasonable than those of Wiberg[29], and we do not obtain the very deep total energies and the poor heats of atomization which result from the CNDO/2 method.

Table (7)

Variation of Energy at Different Bond Lengths

(Bond length in A° and energy in a.u.)

Name of Molecule	Variation of Bond	Bond Length	ENERGY i) CNDOR	ENERGY ii) CNDO/2
Methane	R_{C-H}	1.324	- 9.0072	- 9.9252
		1.224	- 9.0749	-10.0555
		1.174	- 9.0830	-10.0965
		1.124	- 9.0674	-10.1154
		1.090	- 9.0402	-10.1126
		0.924	- 8.6281	- 9.8374
Ethane (R_{C-H} = 1.128 fixed)	R_{C-C}	1.706	-16.6501	-18.7414
		1.606	-16.6759	-18.7911
		1.506	-16.6823	-18.8191
		1.406	-16.6640	-18.8195
		1.306	-16.6009	-18.7726
Ethane (R_{C-C} = 1.506 fixed)	R_{C-H}	1.328	-16.6146	-18.5485
		1.228	-16.7055	-18.7356
		1.128	-16.6823	-18.8191
		1.028	-16.4887	-18.7429
		0.928	-16.0272	-18.4147

Table (7) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	ENERGY i) CNDOR	ENERGY ii) CNDO/2
C_2H_4	$R_{C=C}$	1.556	-15.1122	-16.9460
(R_{C-H} =		1.456	-15.1645	-17.0224
1.119		1.356	-15.1893	-17.0634
fixed)		1.256	-15.1682	-16.9882
		1.156	-15.0777	
C_2H_4	R_{C-H}	1.300	-15.1561	-16.9125
($R_{C=C}$ =		1.250	-15.1891	
1.356		1.220	-15.2014	
fixed)		1.180	-15.2077	
		1.150	-15.2032	
		1.130	-15.1952	-17.0657
		1.125	-15.1929	-17.0665
		1.115	-15.1868	-17.0675
		1.110	-15.1833	-17.0676
		1.100	-15.1752	-17.0670
Acetylene	$R_{C\equiv C}$	1.439	-13.5651	-15.1677
(R_{C-H} =		1.339	-13.6478	-15.2756
1.103		1.239	-13.6892	-15.3377
fixed)		1.205	-13.6717	-15.3411
		1.139	-13.6634	-15.3296
		1.039	-13.5352	-15.2187

Table (7) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	ENERGY i) CNDOR	ENERGY ii) CNDO/2
Acetylene	R_{C-H}	1.303	-13.6532	-15.2394
($R_{C\equiv C}$ =		1.203	-13.6899	-15.3066
1.239		1.103	-13.6892	-15.3377
fixed)		1.059	-13.6718	-15.3348
		1.003	-13.6297	-15.3116
		0.903	-13.4811	-15.1989
Allene	$R_{C=C}$	1.542	-21.1754	
(R_{C-H} =		1.442	-21.2767	-23.9522
1.120		1.342	-21.3059	-24.0257
fixed)		1.312	-21.2847	-24.0420
		1.242	-21.2675	-24.0186
Allene	R_{C-H}	1.320	-21.2763	
($R_{C=C}$ =		1.220	-21.3391	-23.9797
1.342		1.120	-21.3059	-24.0257
fixed)		1.020	-21.1944	-23.9891

Table (7) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	ENERGY i) CNDOR	ENERGY ii) CNDO/2
Propane	R_{C-C}	1.413	-24.1478	-27.4965
(R_{C-H} =		1.513	-24.1965	-27.5000
1.09		1.526	-24.2052	-27.4956
fixed)		1.540	-24.2004	-27.4906
		1.613	-24.1923	-27.4454
		1.713	-24.1492	-27.3490
Butane	R_{C-C}	1.413	-31.1832	-35.8213
(R_{C-H} =		1.513	-31.7655	-36.1940
1.09		1.526	-31.7699	-36.1884
fixed)		1.540	-31.7729	-36.1805
		1.613	-31.7642	-36.1139
		1.713	-31.7029	-35.9702
Butane	R_{C-H}	1.09	-31.7729	-36.1805
(R_{C-C} =		1.19	-31.9129	-36.1310
1.540		1.29	-31.8348	-35.8785
fixed)				

Table (7) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	ENERGY i) CNDOR	ENERGY ii) CNDO/2
Benzene	$R_{C\cdots C}$	1.623	-40.8871	-46.4775
(R_{C-H} =		1.523	-41.1229	-46.8653
1.09		1.423	-41.2036	-47.0838
fixed)		1.397	-41.1882	-47.1015
		1.223	-40.4664	-46.5940

Variation of Energy with C-C bond lengths (Fig. 8, 9, 10, 11, 12, 13, 14) and C-H bond lengths (Fig. 7, 8A, 9A, 10A, 11A, 13A) in CNDOR and CNDO/2 Methods.

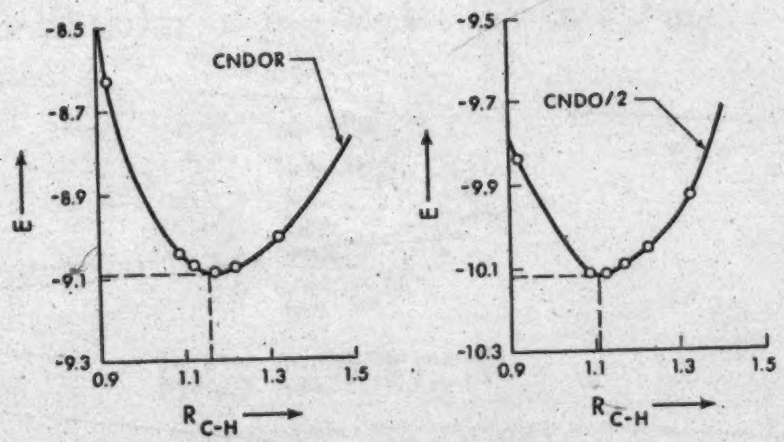


Fig. 7 (Methane)

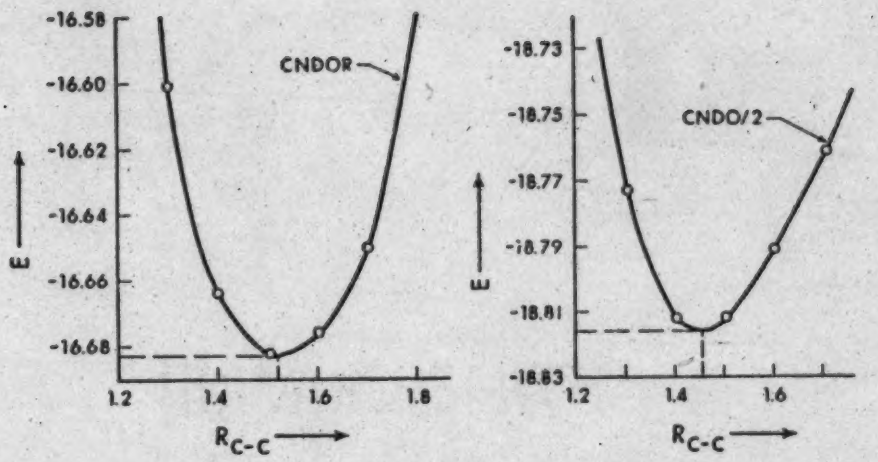


Fig. 8 (Ethane)

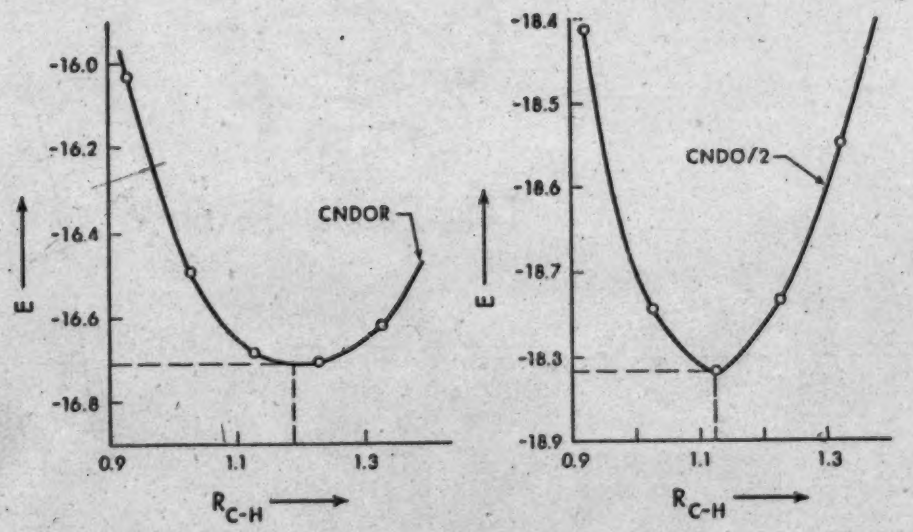


Fig. 8A (Ethane)

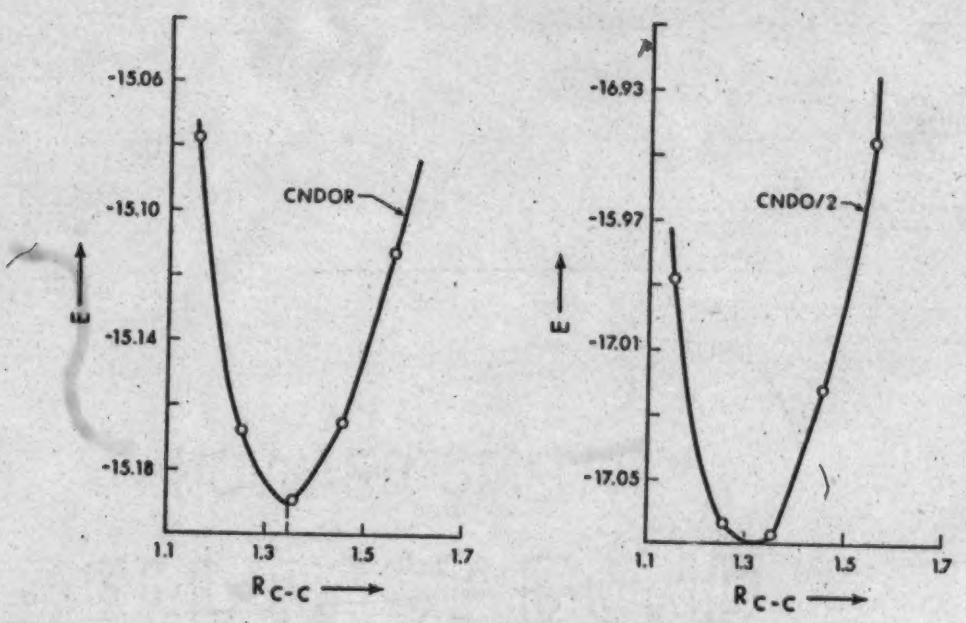


Fig. 9 (Ethylene)

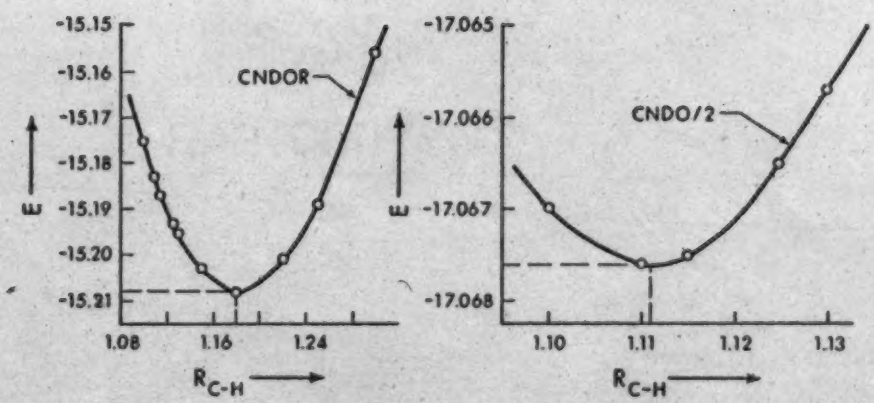


Fig. 9A (Ethylene)

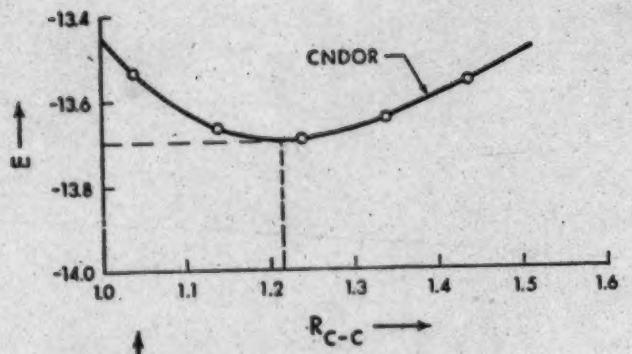
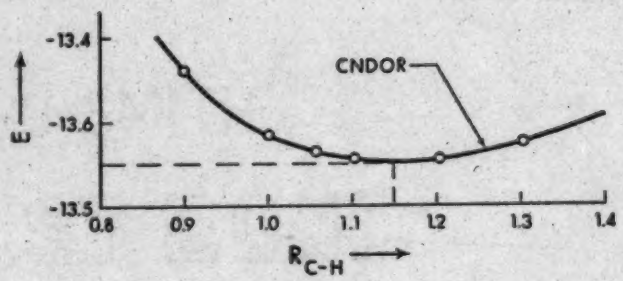


Fig.10 (Acetylene)



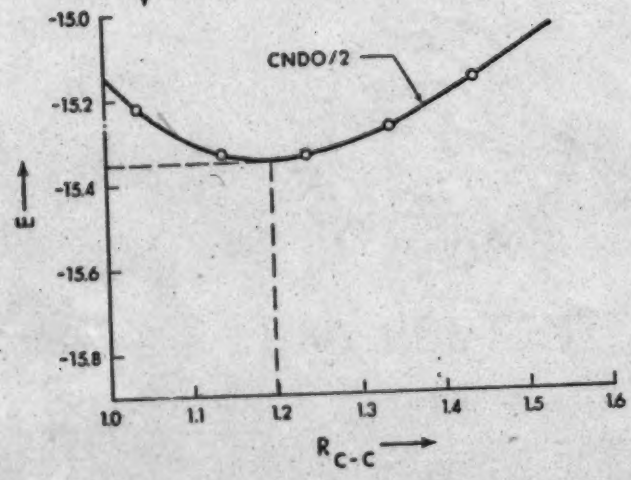
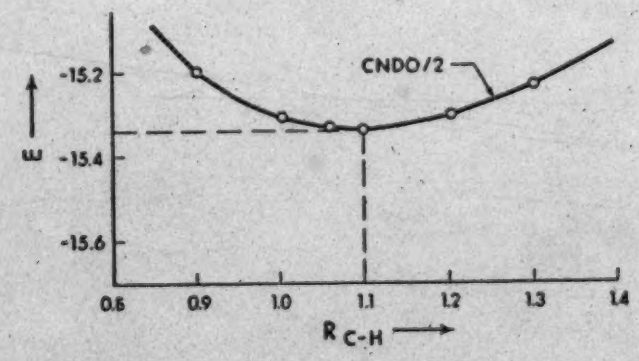


Fig.10A (Acetylene)



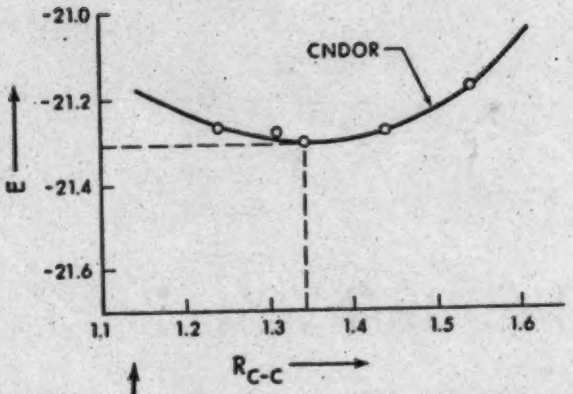


Fig.11 (Allene)

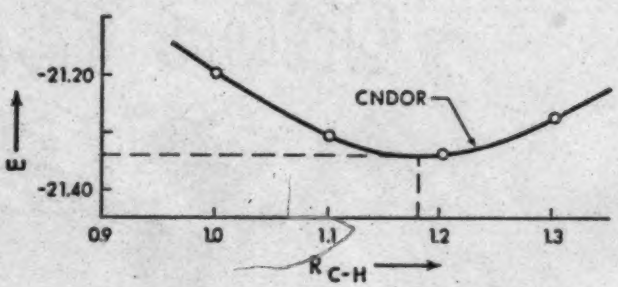
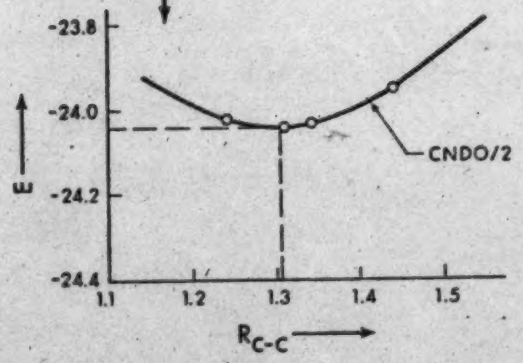
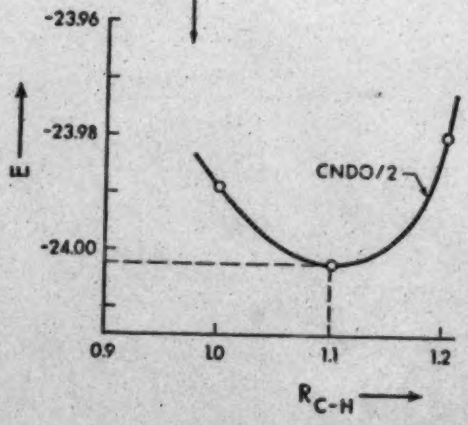
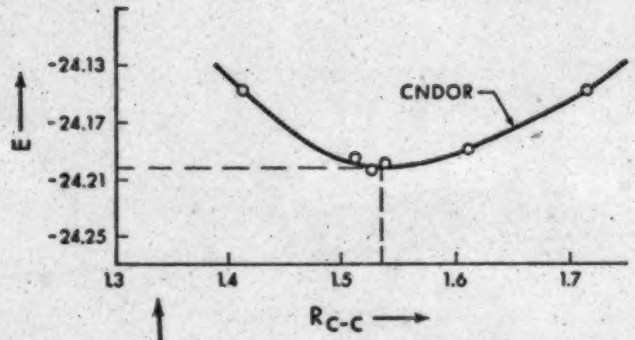


Fig. 11A (Allene)







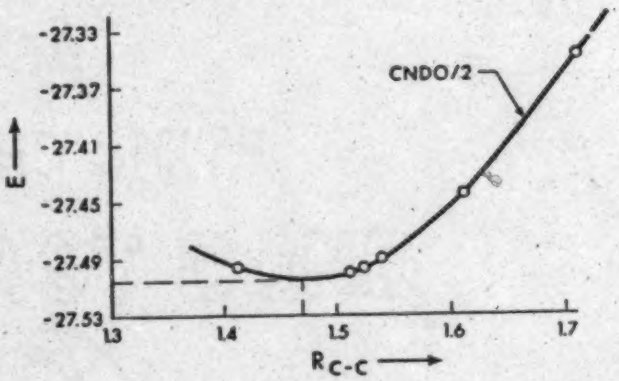


Fig. 12 (Propane)

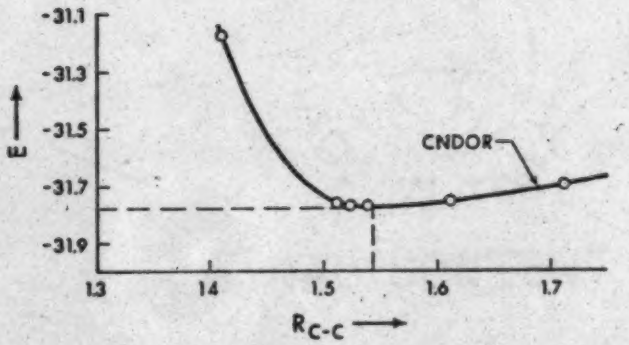
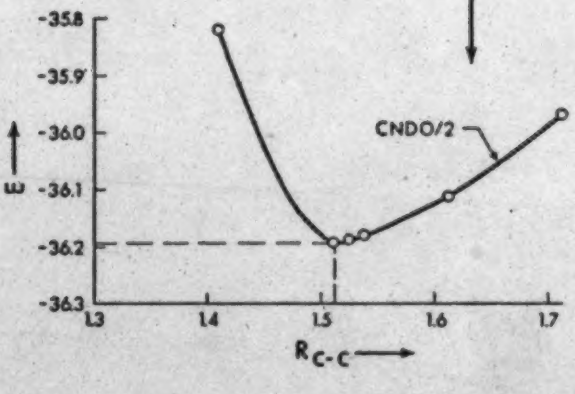


Fig.13 (Butane)



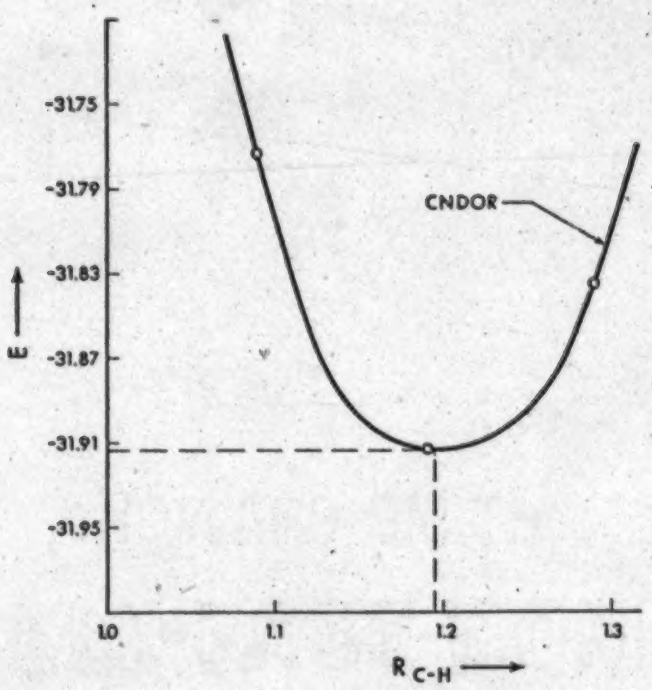


Fig. 13A (Butane)

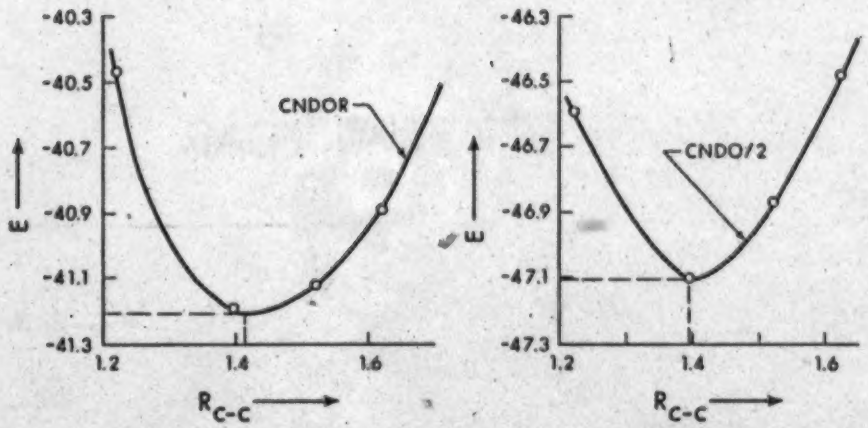


Fig. 14 (Benzene)

Table (8)

Bond Lengths (A°) at the Minimum Energy

Molecule	Bond	Bond Lengths		Bond Lengths From the Figures		Observed[a] Bond Length	Wiberg's[b] Value
		i) CNDOR	ii) CNDO/2	i) CNDOR	ii) CNDO/2		
CH_4	C-H	1.174	1.124	1.160	1.110	1.106[c]	1.124
C_2H_6	C-C	1.506	1.406	1.520	1.457	1.536	1.506
	C-H	1.228	1.128	1.19	1.124	1.107	1.128
C_2H_4	C=C	1.356	1.356	1.346	1.313	1.332	1.356
	C-H	1.130	1.115	1.18	1.110	1.084	1.120
C_2H_2	C≡C	1.239	1.205	1.215	1.197	1.205	1.239
	C-H	1.203	1.059	1.15	1.10	1.059	1.103
C_3H_4	C=C	1.342	1.312	1.342	1.305	1.312	1.342
	C-H	1.220	1.082	1.18	1.1	1.084	1.120
C_3H_8	C-C	1.526	1.513	1.535	1.47	1.526[d]	1.513
	C-H	1.19	1.09			1.09	
C_4H_{10}	C-C	1.54	1.513	1.545	1.513	1.539	
	C-H	1.19	1.09			1.1	
C_6H_6	C⋯C	1.423	1.397	1.415	1.397	1.397	1.423

(a) From Ref. Interatomic Distances, Chem. Soc. Special Publ. No. 18 London (1965)

(b) From Ref. (29) (c) From Ref. (38) (d) From Ref. (39)

B. CNDOK Method:

Table (9) contains the energy values for all the molecules studied. Table (10) contains the energies calculated using different bond lengths. Figures are drawn to show the variation of energy with bond lengths (Figures 15-22). Bond lengths for which the energy is minimum, are included in Table (11) along with observed bond lengths, and the corresponding energy is included in Table (9) which also contains the calculated and observed heats of atomization.

Heats of Atomization:

To compare the heats of atomization with experimental values, they have been calculated in the following way:

$$E(H) = -0.5 \text{ a.u.}$$

$$E(C) = 2U_{2s2s} + 2U_{2p2p} + 6\Gamma_{sp}$$

$$= -2x \frac{51.774}{27.21} -2x \frac{43.295}{27.21} +6x \frac{10.778}{27.21}$$

$$= -4.6112 \text{ a.u.}$$

ΔE_{atom} = Number of 'C' atoms x E(C) +
Number of 'H' atoms x E(H)

$\Delta H_{atom} = \Delta E_{atom}$ - Total Energy

Although the heats of atomization calculated by the CNDOK method do not agree so well with experiment as in the previous method (CNDOR), still the CNDOK method is in much better agreement than the CNDO/2 method.

Table (9)

Comparison of Calculated and Observed Heats of Atomization (a.u.) in CNDOK

Compound	Total Energy	ΔE	ΔH_{atom} (cal.)	ΔH_{atom} (obs.)[a]
CH_4	- 7.3316	- 6.6112	0.7204	0.6693
C_2H_6	-13.498	-12.2223	1.2757	1.1350
C_2H_4	-12.162	-11.2223	0.9397	0.8979
C_2H_2	-10.849	-10.2223	0.6267	0.6478
C_3H_4	-17.004	-15.8335	1.1705	1.1254
C_3H_8	-19.558	-17.8335	1.7245	1.6033
C_4H_{10}	-25.765	-23.4447	2.3203	2.0736
C_6H_6	-33.067	-30.6670	2.400	2.1847

(a) From Ref. (29)

Bond Lengths:

From Table (11) it is evident that bond length obtained by CNDOK method is not so good as in the case of CNDOR. But we should not be discouraged because this method is still in the stage of preliminary parametrization. We hope that after proper parametrization the prediction of bond lengths will be improved.

Table (10)

Variation of Energy with Different Bond Lengths in CNDOK

(Bond length in A°, and Energy in a.u.)

Name of Molecule	Variation of Bond	Bond Length	Energy
Methane	R_{C-H}	1.324	- 7.3060
		1.224	- 7.3316
		1.174	- 7.3202
		1.124	- 7.2875
		1.090	- 7.2503
Ethane	R_{C-C}	1.806	-13.4370
(R_{C-H} =		1.706	-13.4408
1.128		1.606	-13.4309
fixed)		1.406	-13.3299
		1.306	-13.2151
Ethane	R_{C-H}	1.128	-13.4408
(R_{C-C} =		1.19	-13.4930
1.706		1.29	-13.4901
fixed)		1.39	-13.4109

Table (10) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	Energy
Ethylene	$R_{C=C}$	1.356	-12.0874
(R_{C-H} =		1.365	-12.0914
1.119		1.456	-12.1178
fixed)		1.556	-12.1163
Ethylene	R_{C-H}	0.980	-11.8743
($R_{C=C}$ =		1.119	-12.1178
1.456		1.180	-12.1554
fixed)		1.280	-12.1563
		1.380	-12.1068
Acetylene	$R_{C\equiv C}$	1.439	-10.8057
(R_{C-H} =		1.339	-10.8270
1.103		1.239	-10.8058
fixed)		1.205	-10.7590
		1.139	-10.7208
Acetylene	R_{C-H}	1.103	-10.8270
(R_{C-C} =		1.203	-10.8494
1.339		1.303	-10.8383
fixed)		1.403	-10.8061

Table (10) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	Energy
Allene	$R_{C=C}$	1.542	-16.9461
(R_{C-H} =		1.442	-16.9585
1.120		1.342	-16.8939
fixed)		1.242	-16.7453
Allene	R_{C-H}	1.02	-16.8086
($R_{C=C}$ =		1.12	-16.9585
1.442		1.22	-17.0031
fixed)		1.32	-16.9833
		1.42	-16.9226
Propane	R_{C-C}	1.413	-19.3265
(R_{C-H} =		1.513	-19.4650
1.09		1.526	-19.4861
fixed)		1.540	-19.4906
		1.613	-19.5361
		1.713	-19.5549
		1.813	-19.4982
Propane	R_{C-H}	1.09	-19.5549
(R_{C-C} =		1.19	-19.7117
1.713		1.29	-19.7085
fixed)			

Table (10) (Cont'd.)

Name of Molecule	Variation of Bond	Bond Length	Energy
Butane	R_{C-C}	1.413	-24.8774
(R_{C-H} =		1.513	-25.6291
1.09		1.526	-25.6478
fixed)		1.540	-25.6660
		1.613	-25.7299
		1.713	-25.7516
		1.813	-25.4632
Benzene	$R_{C\cdots C}$	1.323	-32.3695
(R_{C-H} =		1.423	-32.8549
1.09		1.523	-33.0489
fixed)		1.623	-33.0463
		1.700	-32.9599

Variation of Energy with C-C and C-H bond lengths (Fig. 15 to 22) in CNDOK Method.

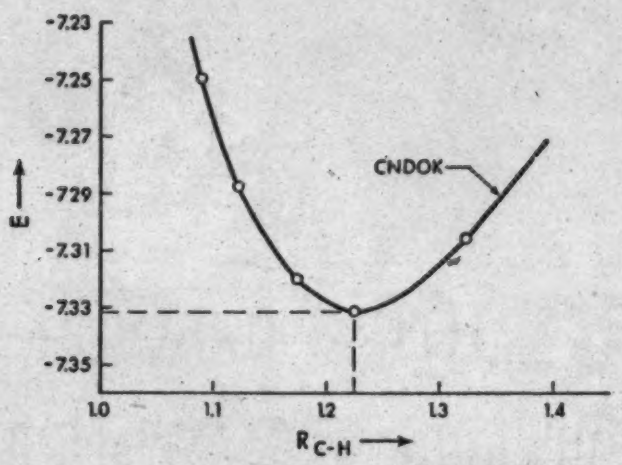


Fig. 15 (Methane)

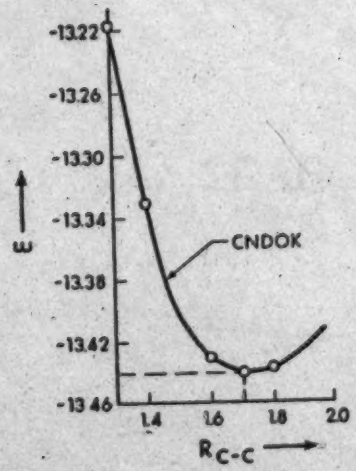


Fig. 16 (Ethane)

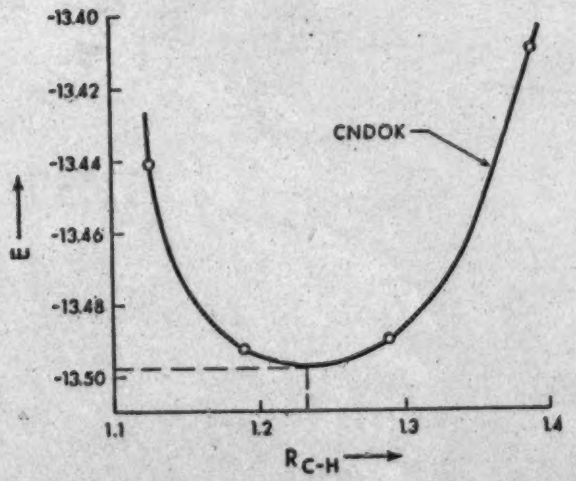


Fig. 16A (Ethane)

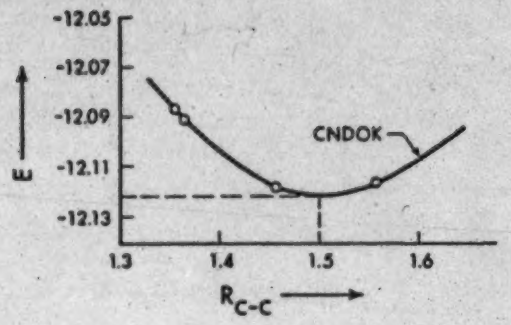


Fig.17 (Ethylene)

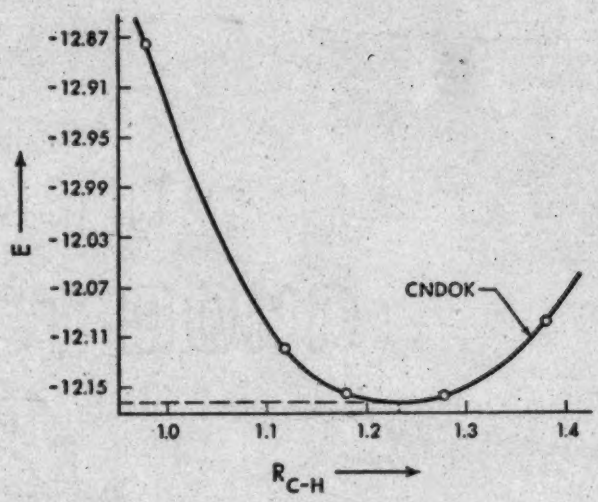


Fig.17A (Ethylene)

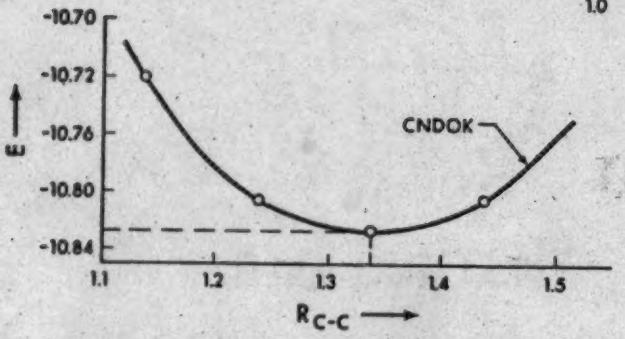


Fig.18 (Acetylene)

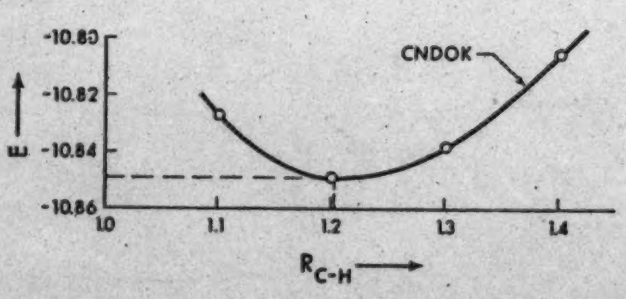


Fig.18A (Acetylene)

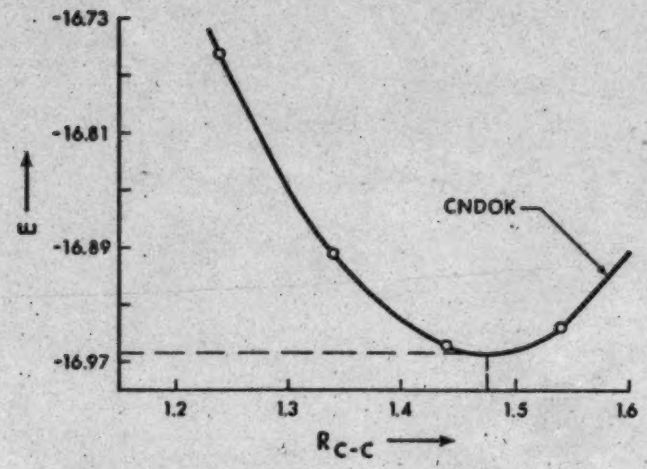


Fig.19 (Allene)

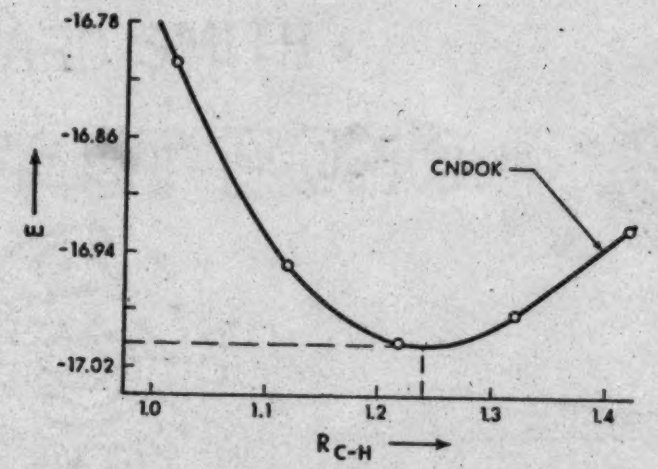


Fig.19A (Allene)

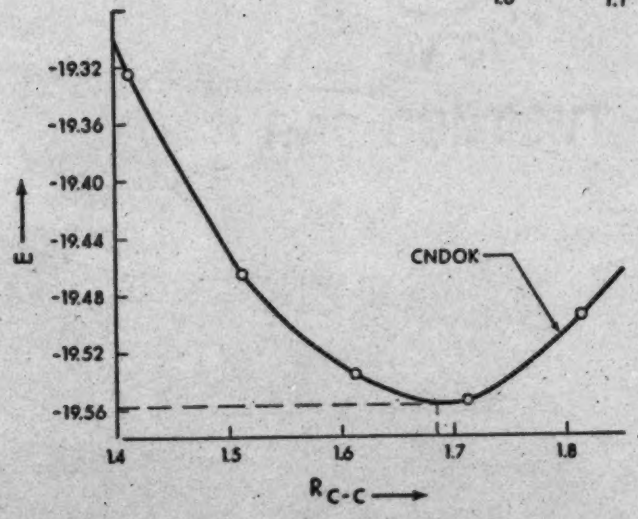


Fig. 20 (Propane)

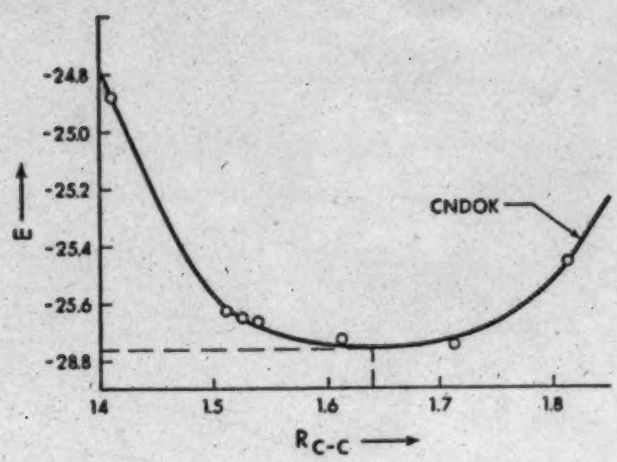


Fig. 21 (Butane)

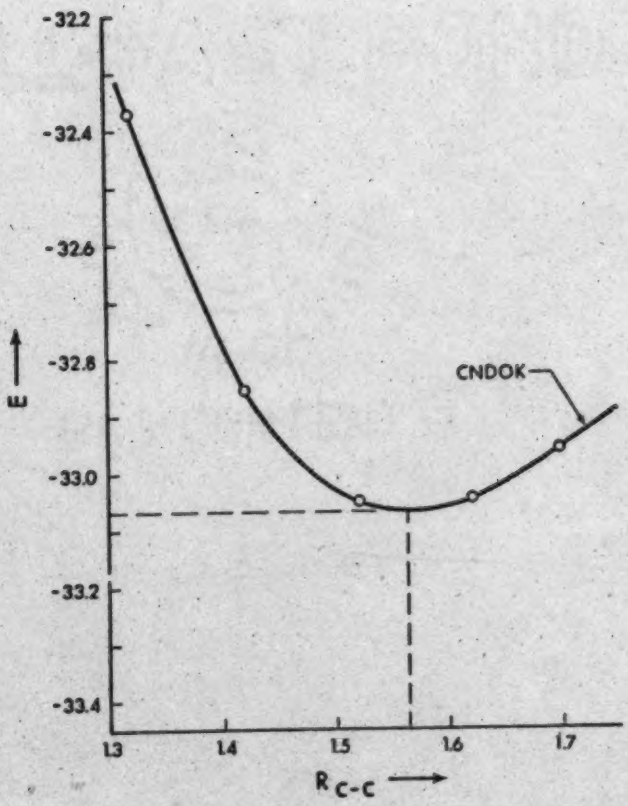


Fig. 22 (Benzene)

Table (11) *

Comparison of Calculated and Observed Bond Lengths in CNDOK

Molecule	Bond	Bond Length	Observed (a)
CH_4	C-H	1.224	1.106 (b)
C_2H_6	C-C	1.706	1.536
	C-H	1.232	1.107
C_2H_4	C=C	1.50	1.332
	C-H	1.232	1.084
C_2H_2	C≡C	1.339	1.205
	C-H	1.203	1.059
C_3H_4	C=C	1.455	1.312
	C-H	1.24	1.084
C_3H_8	C-C	1.685	1.526 (c)
C_4H_{10}	C-C	1.640	1.54
C_6H_6	C-C	1.565	1.397

(a) Interatomic distances, Chem. Soc. Special Publ. No. 18 London (1965).

(b) From Ref. (38).

(c) From Ref. (39).

* Bond length in A°.

C. Conclusion:

In view of the results presented here, we may conclude that good theoretical values for heats of formation can be obtained through the proper parametrization of a CNDO-level semi-empirical theory. The essential point we have brought forward is the importance of the balance between the one-electron energy (negative) and the two-electron energy (positive). Under the ZDO approximation, many terms in the energy formula are eliminated. If there arises any appreciable imbalance due to the effect of these neglected terms between the one- and two-electron parts, then we are bound to have a poor total-energy value. It is our opinion that this has been the case with most of the methods thus far proposed by various authors. We have attempted to maintain the balance by introducing two parameters, λ and ω, in the one-electron part of the diagonal energy matrix elements.

As described earlier, the use of the ZDO approximation was, to some extent, justified by introducing the notion of the orthogonalized atomic orbitals (for example Löwdin's orbitals) in the P-P-P theory but it seems to be difficult to maintain the same logic and subsequent justification in the all-

valence-electron theory. However we keep it as a necessary evil in order to make the calculations feasible for large molecules.

Although the bond lengths calculated by the CNDOK method are not so good as those obtained by CNDO/2 method, the heats of atomization and total-energies are much better than those of the CNDO/2 method. Furthermore, we must emphasize that the CNDOK method does not give bond lengths which are so far afield as to render the method hopeless. On the contrary, we believe that the CNDOK method represents a significant step toward solving Klopman's dilemma. Although in this method we can employ either of the three proposed ways (Roothaan's, Ohno's, or Mataga-Nishimoto's formula) to obtain coulomb integrals, we are not restricted to the use of the particular corresponding values of κ_μ and κ_ν. The flexibility represented by these parameters has yet to be exploited. Even more flexibility can be seen when we consider the effect of also varying λ and ω along with the κ's. The present work has shown that such a parametrization leads to a useful semi-empirical method. Considering that there still remains a considerable amount of the flexibility in the method we can be optimistic about the usefulness of the method in the simultaneous prediction of a variety of molecular properties.

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